

AP\* EDITION

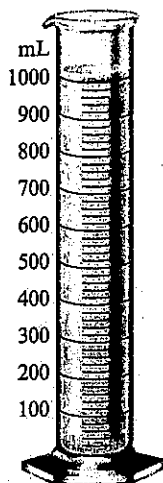
first edition

# Chemistry

Zumdahl  
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## AP Multiple-Choice Review Questions

- When each of the following is heated to 50°C and the temperature is held constant for 5 minutes, which one undergoes *only* a physical change?
  - egg
  - steak
  - ice cream
  - cake batter
- A graduated cylinder contains multiple different liquid layers.



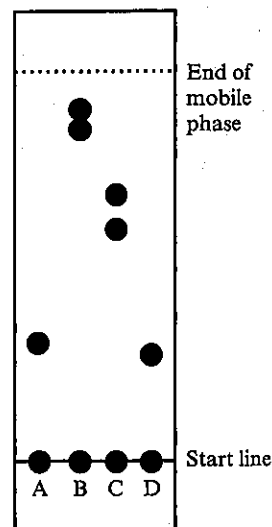
Very small samples are taken from the liquids at various heights and tested for density, viscosity, and boiling point. The data are listed below.

Height (mL)	Density (g/mL)	Viscosity (cP)	Boiling Point (°C)
1000	0.83	0.72	242.4
900	0.83	0.71	242.3
800	1.07	0.93	99.7
700	1.08	0.92	99.8
600	1.08	0.93	99.7
500	2.05	1.86	153.5
400	2.06	1.87	153.5
300	2.05	1.85	153.6
200	2.04	1.86	153.6
100	2.05	1.86	153.5

How many different liquids are present in the graduated cylinder?

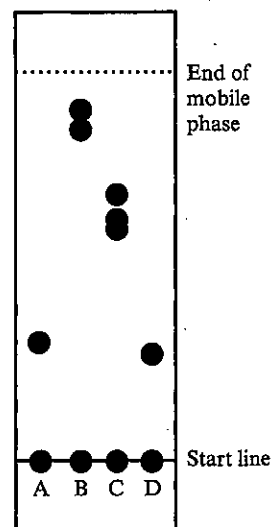
- 1
- 2
- 3
- 4

- Four different kinds of inks are placed on chromatography paper, and a solvent is introduced and allowed to move up the paper.



From the diagram shown above, which two inks are likely to contain molecules that have the most similar molecular structures?

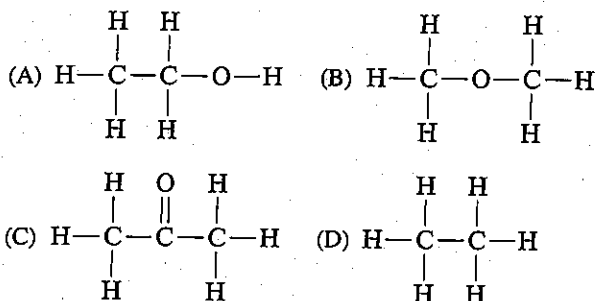
- A and D
  - B and D
  - B and C
  - A and C
- Four different inks are placed on chromatography paper, and a solvent is introduced and allowed to move up the paper.



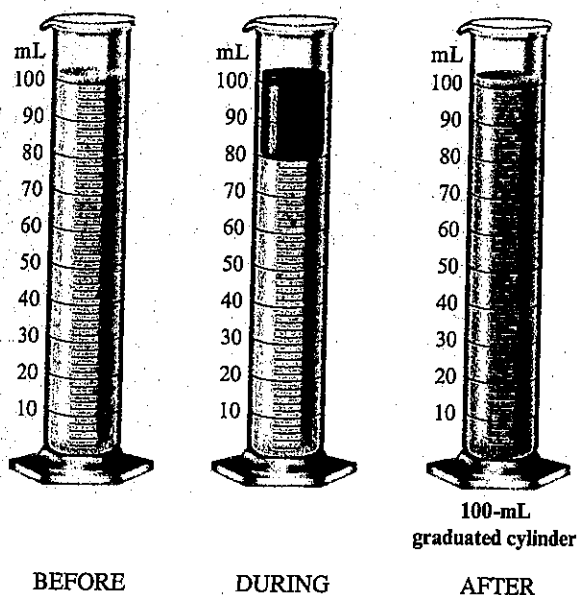
From the diagram shown above, which ink contains a component likely to have a molecular structure most similar to that of the solvent?

- A
- B
- C
- D

5. Four substances with the following structures are placed on chromatography paper with water as the mobile phase. The paper is allowed to touch the water. After an hour, which substance will have moved the farthest on the paper? Water consists of  $\text{H}-\text{O}-\text{H}$  molecules.



The following diagram is used for questions 6–8.



A 100-mL graduated cylinder is filled with 100 mL of water. A few drops of food coloring are added to the top of the water, without mixing. Initially, the top of the graduated cylinder appears to be very dark, while the bottom remains clear and colorless. After 5 minutes the liquid in the graduated cylinder appears to be uniformly colored.

6. Classify the contents in the graduated cylinder before any food coloring is added.
- element
  - compound
  - heterogeneous mixture
  - homogeneous mixture

7. Classify the contents in the graduated cylinder just after the food coloring is added.

- element
- compound
- heterogeneous mixture
- homogeneous mixture

8. Classify the contents in the graduated cylinder after the 5 minutes has elapsed.

- element
- compound
- heterogeneous mixture
- homogeneous mixture

9. Several of Jupiter's moons are believed to have a liquid layer, possibly water, below their icy surfaces. NASA and the European Space Agency are planning several interplanetary probes that will visit the moons of Jupiter. It has been suggested that a probe could land on one of the moons and drill through the surface of ice to the liquid layer. The probe would then sample the liquid at five different depths. Why will the probe test the liquid at five different depths?

- to determine whether the liquid layer is water
- to determine whether the liquid layer could support life
- to determine the chemical composition of the liquid layer
- to determine whether the liquid layer is a homogeneous solution or heterogeneous mixture

10. A 10.00-g piece of metal is submerged in a graduated cylinder initially containing 20.00 mL of water. With the metal in the cylinder, the level of the water is recorded as 21.40 mL. Determine the identity of the metal.

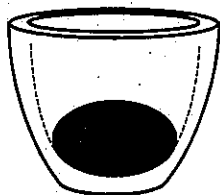
- aluminum (density = 2.70 g/mL)
- zinc (density = 7.13 g/mL)
- silver (density = 10.49 g/mL)
- gold (density = 19.32 g/mL)

## AP Multiple-Choice Review Questions

- Which of the following combinations of elements is likely to produce an ionic bond?
  - Li and Cl
  - Li and Rb
  - N and S
  - N and O
- When 20.0 g of solid calcium carbonate is placed into a crucible and heated, it will decompose into 11.2 g of solid calcium oxide and carbon dioxide gas. There are several ways to represent this reaction. One of the most common is by a chemical equation, shown here:



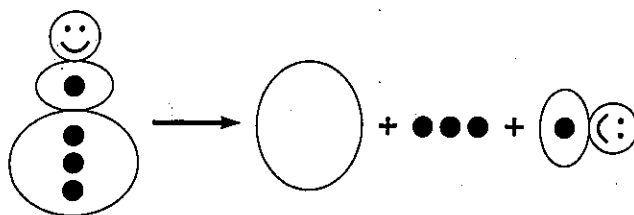
Another way is to draw it. The crucible shown below illustrates what it looks like before any reaction has taken place. What will the crucible look like after the reaction has taken place?



20.0 g  $\text{CaCO}_3(s)$

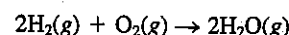
- 8.8 g
  - 11.2 g
  - 31.2 g
  - 8.8 g
- When fossil fuels are burned, carbon is released into the air in the form of carbon dioxide ( $\text{CO}_2$ ) gas. Carbon dioxide is known as a greenhouse gas, because it traps heat in the atmosphere and has been implicated as a contributor to global warming. One method of reducing global warming is to plant trees. What role do trees play in reducing global warming?
    - Trees absorb carbon dioxide and use the carbon to grow.
    - Trees absorb sunlight as they grow, reducing the temperature.
    - Trees produce oxygen, which reacts with the carbon dioxide in the air.
    - Tree leaves reflect the sun's light back into space, thus less is available to heat up the atmosphere.

4.

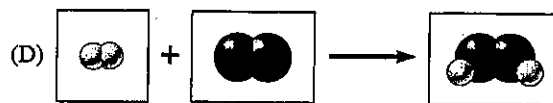
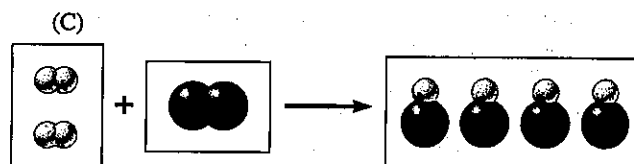
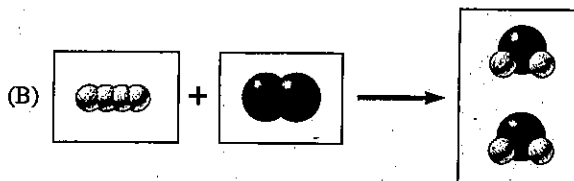
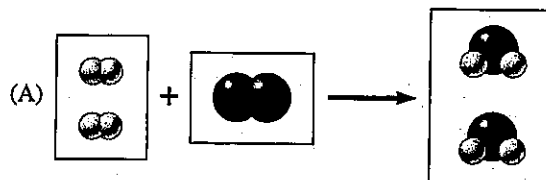


The diagram shown above best represents which of the following?

- Dalton's atomic theory
  - law of definite proportions
  - law of multiple proportions
  - law of conservation of mass
- Consider the reaction between hydrogen ( $\text{H}_2$ ) gas and oxygen ( $\text{O}_2$ ) gas to form water ( $\text{H}_2\text{O}$ ).



Which of the following is a correct representation of this reaction?



- Which of the following equations satisfies the law of conservation of mass?

- $\text{H}_2(g) + \text{O}_2(g) \rightarrow \text{H}_2\text{O}(g)$
- $\text{Na}(s) + \text{Cl}_2(g) \rightarrow \text{NaCl}(s)$
- $\text{N}_2(g) + \text{H}_2(g) \rightarrow \text{NH}_3(g)$
- $\text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g)$

7. The following data were collected for several compounds of nitrogen and oxygen:

W	0.5711 g
X	1.142 g
Y	2.284 g
Z	2.855 g

These data support which of the following?

- (A) Hess's law  
(B) law of definite proportions  
(C) law of multiple proportions  
(D) law of conservation of mass
8. The following data were collected for several compounds of nitrogen and oxygen:

W	0.5711 g
X	1.142 g
Y	2.284 g
Z	2.855 g

If compound X has an equal number of oxygen and nitrogen atoms, what is the most likely formula for compound Y?

- (A) NO  
(B) NO<sub>2</sub>  
(C) N<sub>2</sub>O  
(D) N<sub>2</sub>O<sub>5</sub>
9. When two elements form a series of compounds, the ratios of the masses of the second element that combine with 1 gram of the first element can always be reduced to small whole numbers. This is known as
- (A) Avogadro's hypothesis  
(B) law of definite proportions  
(C) law of multiple proportions  
(D) law of conservation of mass
10. Which of the following choices consists of a pair of isotopes?
- (A) <sup>14</sup>C and <sup>14</sup>N  
(B) <sup>23</sup>Na and <sup>23</sup>Na<sup>+</sup>  
(C) <sup>2</sup>H and <sup>1</sup>H  
(D) <sup>35</sup>Cl and <sup>35</sup>Cl<sup>-</sup>
11. What is the correct name for CaCl<sub>2</sub>?
- (A) calcium chloride  
(B) calcium chlorine  
(C) calcium chlorite  
(D) calcium(II) chloride

12. What is the correct name for Fe<sub>2</sub>S<sub>3</sub>?

- (A) diiron trisulfide  
(B) iron sulfide  
(C) iron(II) sulfide  
(D) iron(III) sulfide

13. What is the correct name for NO<sub>2</sub>?

- (A) nitrite  
(B) nitrogen oxide  
(C) nitrogen dioxide  
(D) dinitrogen monoxide

14. What is the name of an aqueous solution that contains HNO<sub>2</sub>?

- (A) nitric acid  
(B) nitrous acid  
(C) hydrogen nitrite  
(D) hydrogen nitrogen dioxide

The following information is used for Questions 15 and 16.

A 20.0-g sample of a hydrated compound is placed into a crucible and heated. The data table for this laboratory investigation is shown below.

Mass of crucible	15.5867 g
Mass of crucible and hydrated sample	19.7644 g
Mass of crucible and anhydrous sample after first heating	18.4388 g
Mass of crucible and anhydrous sample after second heating	18.0244 g
Mass of crucible and anhydrous sample after third heating	18.0242 g

15. Why can we conclude that all of the water of hydration has been removed?

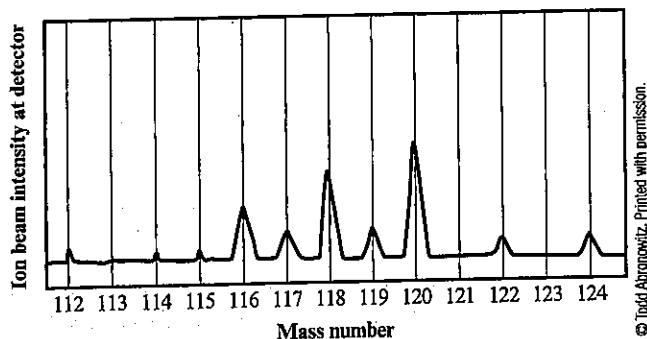
- (A) The mass of the crucible and sample increased then decreased.  
(B) The mass of the crucible and sample decreased after each heating.  
(C) The mass of the crucible and sample decreased due to the water of hydration being "driven off" by the heating.  
(D) The mass of the crucible and sample remained relatively constant after the second heating.

16. What is the mass of the water of hydration in the hydrate?

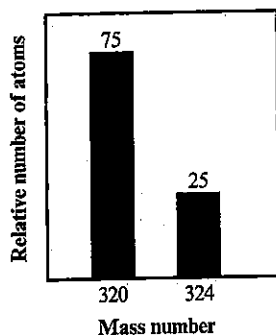
- (A) 0.4146 g  
(B) 1.7402 g  
(C) 2.4325 g  
(D) 4.1777 g

## AP Multiple-Choice Review Questions

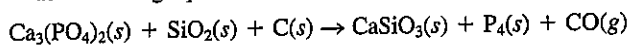
1. When a sample of an unknown element is vaporized and injected into a mass spectrometer, the results shown below are obtained. Use these data to estimate the average atomic mass of this element.



- (A) 117 amu  
 (B) between 117 and 118 amu  
 (C) between 118 and 119 amu  
 (D) between 119 and 120 amu
2. An unnamed element with an atomic number of 130 is vaporized and injected into a mass spectrometer. The results are shown below. Use these data to calculate the average atomic mass of this element.



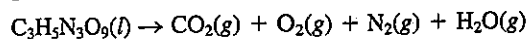
- (A) 320 amu  
 (B) 321 amu  
 (C) 322 amu  
 (D) 324 amu
3. Phosphorus can be produced by reacting calcium phosphate, silicon dioxide, and carbon at high temperatures according to the following equation:



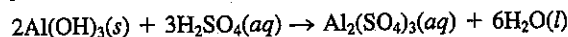
What is the sum of the coefficients when the equation is balanced in standard form (lowest multiple whole numbers)?

- (A) 16  
 (B) 25  
 (C) 32  
 (D) 35

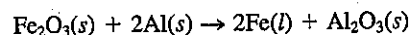
4. Nitroglycerine,  $\text{C}_3\text{H}_5\text{N}_3\text{O}_9$ , explodes with tremendous force due to the numerous gaseous products. The *unbalanced* equation for the explosion of nitroglycerine is shown below. What is the coefficient of the  $\text{CO}_2(g)$  when the equation is balanced using the lowest whole number coefficients?



- (A) 8  
 (B) 10  
 (C) 12  
 (D) 14
5. The simplest formula for a compound made from element X (molar mass = 79.0 g/mol) that is 21.0% nitrogen by mass is
- (A)  $\text{XN}$   
 (B)  $\text{XN}_2$   
 (C)  $\text{X}_2\text{N}_3$   
 (D)  $\text{X}_3\text{N}_2$
6. When 78.0 g of aluminum hydroxide,  $\text{Al}(\text{OH})_3$  (molar mass = 78.0 g/mol), reacts with 49.0 g sulfuric acid,  $\text{H}_2\text{SO}_4$  (molar mass = 98.1 g/mol), what mass of water is produced? The equation is



- (A) 18.0 g  
 (B) 36.0 g  
 (C) 54.0 g  
 (D) 127 g
7. What mass of aluminum is required if 40.0 g of iron(III) oxide,  $\text{Fe}_2\text{O}_3$ , is to be completely consumed as shown in the following reaction?



- (A) 13.5 g  
 (B) 27.0 g  
 (C) 40.0 g  
 (D) 67.0 g
8. The mineral magnesite contains magnesium carbonate,  $\text{MgCO}_3$  (molar mass = 84 g/mol), and other impurities. When a 1.26-g sample of magnesite was dissolved in hydrochloric acid, 0.22 g of  $\text{CO}_2$  was generated. If the magnesite contained no carbonate other than  $\text{MgCO}_3$ , what was the percent  $\text{MgCO}_3$  by mass in the magnesite? The equation is



- (A) 25%  
 (B) 33%  
 (C) 50%  
 (D) 67%
9. A compound is analyzed and found to contain 1.30 moles of Na, 0.65 moles of Te, and 2.60 moles of O. What is the simplest formula of this compound?
- (A)  $\text{NaTeO}_2$   
 (B)  $\text{Na}_2\text{TeO}_4$   
 (C)  $\text{Na}_2\text{Te}_2\text{O}$   
 (D)  $\text{Na}_2\text{Te}_4\text{O}$

10. The average atomic mass of a chlorine atom is 35.45 amu. Chlorine consists of two isotopes,  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ . Which of the following most closely approximates the relative abundance of these isotopes?
- (A) 25%  $^{35}\text{Cl}$  and 75%  $^{37}\text{Cl}$   
(B) 50%  $^{35}\text{Cl}$  and 50%  $^{37}\text{Cl}$   
(C) 75%  $^{35}\text{Cl}$  and 25%  $^{37}\text{Cl}$   
(D) 90%  $^{35}\text{Cl}$  and 10%  $^{37}\text{Cl}$
11. What is the sum of the coefficient integers when the following equation is balanced in standard form (lowest multiple whole numbers)?
- $$\text{FeCr}_2\text{O}_7(s) + \text{K}_2\text{CO}_3(s) + \text{O}_2(g) \rightarrow \text{K}_2\text{CrO}_4(s) + \text{Fe}_2\text{O}_3(s) + \text{CO}_2(g)$$
- (A) 9  
(B) 15  
(C) 24  
(D) 31
12. When iron(III) oxide is heated with carbon, the products are iron metal and carbon monoxide. Balance the equation in standard form and determine the sum of the coefficients.
- (A) 4  
(B) 5  
(C) 6  
(D) 9
13. Methanol ( $\text{CH}_3\text{OH}$ ) can react with oxygen gas to produce formaldehyde ( $\text{H}_2\text{CO}$ ) and water. How much formaldehyde can be produced by reacting 4.0 moles of methanol with 4.0 moles of oxygen gas?
- (A) 2.0 moles  
(B) 4.0 moles  
(C) 6.0 moles  
(D) 8.0 moles
14. Which of the following compounds contains the greatest percent by mass of nitrogen?
- (A)  $\text{NH}_3$   
(B)  $\text{HCN}$   
(C)  $\text{N}_2\text{O}$   
(D)  $\text{NI}_3$
15. Substance  $\text{AB}_2$  is 60.0% A by mass. What is the percent A by mass for substance  $\text{AB}$ ?
- (A) 20.0%  
(B) 40.0%  
(C) 60.0%  
(D) 75.0%
16. In a Bunsen burner, methane reacts with oxygen to produce carbon dioxide and water, as shown in the balanced equation below:
- $$\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g)$$
- What mass of water can be produced from 16 grams of methane and excess oxygen?
- (A) 8.0 g  
(B) 16 g  
(C) 18 g  
(D) 36 g
17. Which of the following reaction mixtures would produce the greatest amount of product, assuming all went to completion? Each involves the reaction symbolized by the equation:
- $$\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$$
- (A) 2 mol  $\text{N}_2$  and 4 mol  $\text{H}_2$   
(B) 1 mol  $\text{N}_2$  and 5 mol  $\text{H}_2$   
(C) 4 mol  $\text{N}_2$  and 2 mol  $\text{H}_2$   
(D) 5 mol  $\text{N}_2$  and 1 mol  $\text{H}_2$

## AP Multiple-Choice Review Questions

Use the following information to answer questions 1 and 2.

For a laboratory investigation, a student is instructed to place a 2.4-g sample of magnesium ribbon into 500 mL of a 2.0 M solution of hydrochloric acid. The student then records the following observations:

- The magnesium ribbon is a bright, shiny, silvery metal.
- The hydrochloric acid is clear and colorless with no detectable odor.
- As soon as the magnesium ribbon is dropped into the hydrochloric acid:
  - bubbles form,
  - a sizzling sound is heard, and
  - a clear, colorless gas with no detectable odor appears to be coming from the reaction vessel.
- After 32 seconds, the magnesium ribbon has completely disappeared.
- There appears to be only a clear, colorless solution after the reaction has taken place.

1. What is the balanced chemical equation for this reaction?

- $\text{Mg} + \text{HCl} \rightarrow \text{MgCl} + \text{H}$
- $\text{Mg} + 2\text{HCl} \rightarrow \text{MgH}_2 + \text{Cl}_2$
- $\text{Mg} + 2\text{HCl} \rightarrow \text{MgCl}_2 + \text{H}_2$
- $\text{Mg} + 2\text{HCl} \rightarrow \text{Mg} + \text{Cl}_2 + \text{H}_2$

2. Identify which substance is being oxidized and which substance is being reduced in this laboratory investigation.

- Magnesium is being oxidized, and the chloride ion is being reduced.
- Magnesium is being reduced, and the chloride ion is being oxidized.
- Magnesium is being oxidized, and the hydrogen ion is being reduced.
- Magnesium is being reduced, and the hydrogen ion is being oxidized.

3. If 200. mL of 0.60 M  $\text{MgCl}_2(aq)$  is added to 400. mL of distilled water, what is the concentration of  $\text{Mg}^{2+}(aq)$  and  $\text{Cl}^-(aq)$  in the resulting solution? (Assume volumes are additive.)

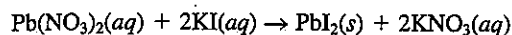
(A)	0.20	0.20
(B)	0.20	0.40
(C)	0.40	0.40
(D)	2.0	2.5

4. Determine the volume of distilled water that should be **added** to 20.0 mL of 12.0 M  $\text{HCl}(aq)$  in order to prepare a 0.500 M  $\text{HCl}(aq)$  solution.

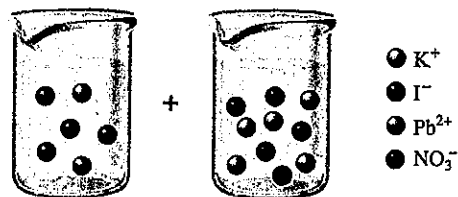
120. mL
140. mL
460. mL
480. mL

Use the following information to answer questions 5 and 6.

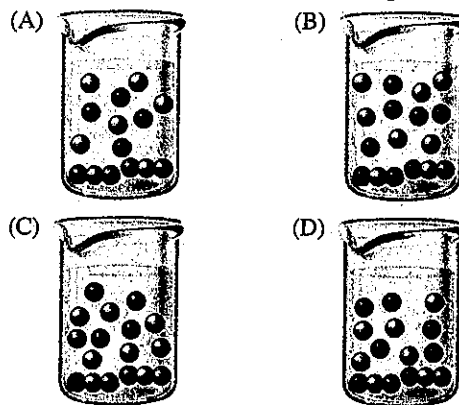
Solutions of lead(II) nitrate and potassium iodide react according to the following equation:



A molecular-level representation illustrating solutions of the reactants lead(II) nitrate and potassium iodide is shown below.



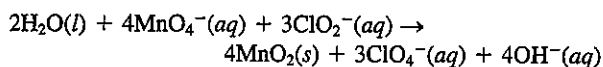
5. Which of the following would be the best molecular-level representation after the reaction has taken place?



6. Which species acts exclusively as spectator ions in this reaction?

- $\text{K}^+$  and  $\text{NO}_3^-$
- $\text{Pb}^{2+}$  and  $\text{I}^-$
- $\text{K}^+$  and  $\text{Pb}^{2+}$
- $\text{I}^-$  and  $\text{NO}_3^-$

7. What is the molarity of a solution containing  $\text{ClO}_2^-(aq)$  if 15 mL of the solution is needed to react completely with 20. mL of 0.20 M  $\text{KMnO}_4$  solution? The balanced equation is



- 0.10 M
- 0.20 M
- 0.30 M
- 0.40 M

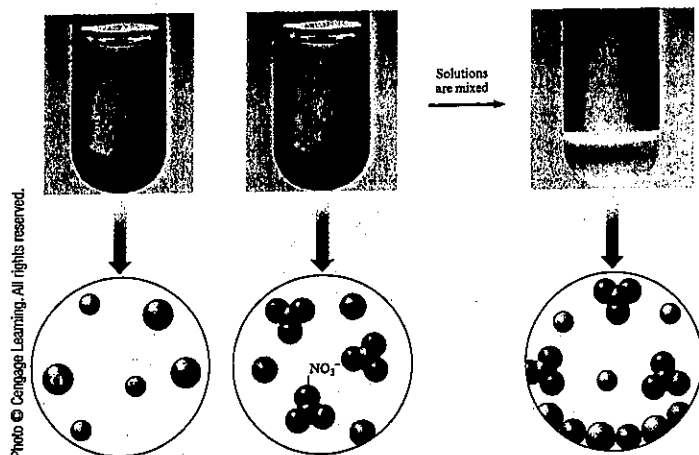
8. A sample of 25.0 mL of 0.120 M  $\text{Ca}(\text{OH})_2(aq)$  is titrated with 0.150 M  $\text{HCl}(aq)$ . What volume of  $\text{HCl}(aq)$  is needed to completely neutralize the  $\text{Ca}(\text{OH})_2(aq)$ ?

- 20.0 mL
- 40.0 mL
- 60.0 mL
- 80.0 mL



Use the following information to answer questions 9 and 10.

The photos of a reaction along with the molecular-level representations are shown below.



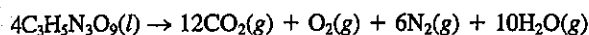
9. What is the correct balanced net ionic equation for the reaction illustrated?
- $\text{KCl} + \text{AgNO}_3 \rightarrow \text{KNO}_3 + \text{AgCl}$
  - $\text{K}^+ + \text{NO}_3^- \rightarrow \text{KNO}_3$
  - $\text{Ag}^+ + \text{NO}_3^- \rightarrow \text{AgNO}_3$
  - $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}$
10. Which species are the spectator ions in this reaction?
- $\text{K}^+$  and  $\text{NO}_3^-$
  - $\text{K}^+$  and  $\text{Cl}^-$
  - $\text{Ag}^+$  and  $\text{NO}_3^-$
  - $\text{Ag}^+$  and  $\text{Cl}^-$
11. In which of the following species is the oxidation state for nitrogen the greatest?
- NO
  - $\text{NO}_2$
  - $\text{N}_2\text{O}$
  - $\text{N}_2\text{O}_5$
12. A 1.0 M solution of table salt (NaCl) is considered to be 1.0 M  $\text{Na}^+$  and 1.0 M  $\text{Cl}^-$ . This means table salt is a
- strong electrolyte
  - weak electrolyte
  - nonelectrolyte
  - strong acid
13. Consider 100.0 mL of a 1.00 M solution of NaCl in a beaker. After several days, you test the solution and find that it has a concentration of 1.33 M. How much water must have evaporated?
- 20.0 mL
  - 25.0 mL
  - 75.0 mL
  - 80.0 mL
14. Calculate the concentration of chloride ions when 200.0 mL of 1.00 M sodium chloride is mixed with 300.0 mL of 1.00 M magnesium chloride.
- 1.00 M
  - 1.40 M
  - 1.60 M
  - 2.00 M
15. What volume of 0.2000 M sulfuric acid is required to neutralize 800.0 mL of 0.1000 M potassium hydroxide?
- 200.0 mL
  - 400.0 mL
  - 800.0 mL
  1600. mL

## AP Multiple-Choice Review Questions

- On a cold day near the ocean, it was found that 8 g of an unknown gas occupies a volume that is a little less than 6 L. Based on this information, what is the most likely identity of the unknown gas?
  - CO<sub>2</sub>
  - Ne
  - O<sub>2</sub>
  - CH<sub>4</sub>
- Which of the following gases is expected to behave most ideally at a given temperature and pressure?
  - H<sub>2</sub>O
  - NH<sub>3</sub>
  - Xe
  - He

The following information is used to answer questions 3 and 4.

Nitroglycerine, C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>O<sub>9</sub>, explodes with tremendous force due to the numerous gaseous products. The equation for the explosion of nitroglycerine is:



A scientist conducts an experiment to characterize a bomb containing nitroglycerine. She uses a steel, rigid container for the test.

Volume of rigid steel container	1.00 L
Molar mass of nitroglycerine	227 g/mol
Temperature	300. K
Amount of nitroglycerine tested	227 g
Value for ideal gas constant, $R$	$0.0821 \frac{\text{L atm}}{\text{mol K}}$

- What is the total pressure produced in this explosion?
  - 25.0 atm
  - 52.0 atm
  - 179 atm
  - 435 atm
- In a second experiment, the total pressure is observed to be 58 atm. What is the partial pressure of the water vapor produced?
  10. atm
  20. atm
  30. atm
  40. atm

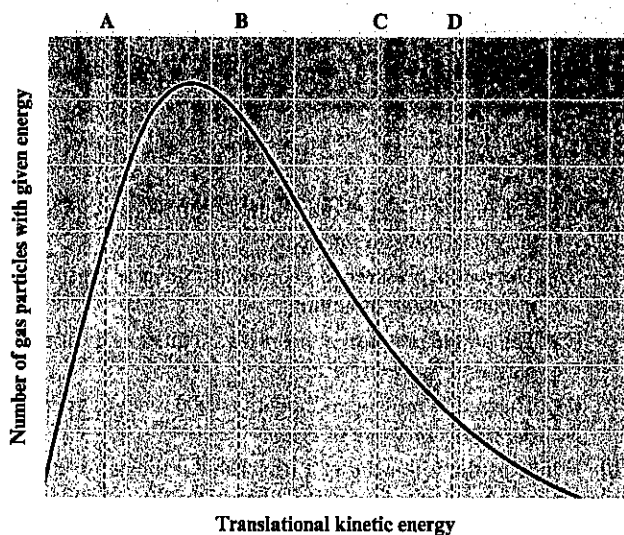
- There are two equations of state commonly used for gas law problems in chemistry: the ideal gas law and the van der Waals equation, both shown in the table below. A sample of 6.00 moles of chlorine gas has a volume of 2.00 L at 273 K. A student is asked to determine the pressure using these two equations.

Equation	$PV = nRT$	$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$
Calculated pressure	67.2 atm	22.5 atm

What is the major factor that accounts for most of the difference in the two values?

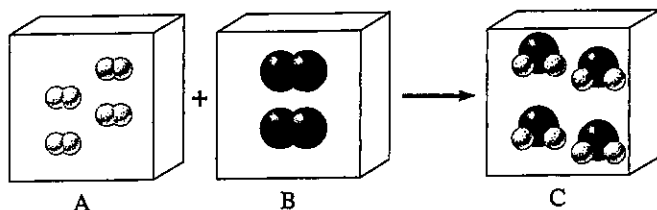
- chlorine is a halogen
  - diatomic nature of chlorine
  - volume of the chlorine particles
  - forces of attraction between chlorine molecules
- A sample of gas is heated from 35°C to 70°C. Which statement correctly describes what happens to the volume?
    - The volume increases by a factor of less than 2.
    - The volume increases by a factor of 2.
    - The volume decreases by a factor of less than 2.
    - The volume decreases by a factor of 2.
  - The Maxwell-Boltzmann distribution for unknown gas is shown. At which point on the graph is the average temperature of the gas most directly related to its translational kinetic energy?

## Maxwell-Boltzmann distribution for an unknown gas



- A
- B
- C
- D

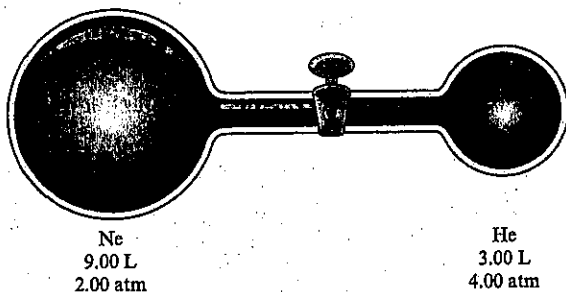
8. Two gases are removed from their original container and placed into a third container, where they react with each other. All three containers have identical volumes, and all gasses are at the same temperature.



Which container has the lowest pressure?

- (A) container A before the reaction  
(B) container B before the reaction  
(C) container C after the reaction  
(D) they all have the same pressure
9. A sample of neon gas is contained in the left-hand bulb and a sample of helium gas is contained in the right-hand bulb of a two-bulb container connected by a valve, as shown in the diagram. Initially the valve is closed.

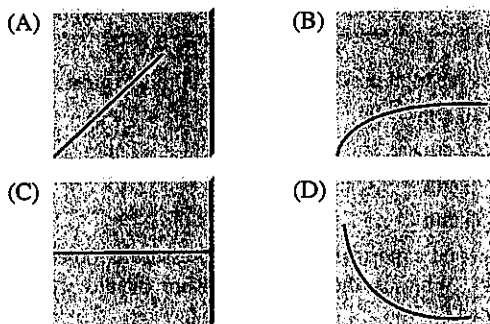
The left-hand bulb has a volume of 9.00 L, and the Ne gas is at a pressure of 2.00 atm. The right-hand bulb has a volume of 3.00 L, and the He gas is at a pressure of 4.00 atm. After the valve is opened, what is true about the relative partial pressures of helium and neon? Assume constant temperature.



- (A) The partial pressure of helium is 1.50 times as great as the partial pressure of neon.  
(B) The partial pressure of neon is 2.00 times as great as the partial pressure of helium.  
(C) The partial pressure of neon is 1.50 times as great as the partial pressure of helium.  
(D) The partial pressure of helium is 2.00 times as great as the partial pressure of neon.
10. Which of the following is a reasonable estimate for the volume of a balloon that has been filled with 300 g of oxygen gas at STP?
- (A) 1 L  
(B) 10 L  
(C) 50 L  
(D) 200 L

11. Which of the following most closely estimates the density of air at 1.0 atm and 25°C to one significant figure?
- (A) 0.1 g/L  
(B) 1 g/L  
(C) 10 g/L  
(D) 100 g/L
12. A certain mass of neon gas is contained in a rigid steel container. The same mass of helium gas is added to this container. Which of the following best describes what happens? Assume the temperature is constant.
- (A) The pressure in the container doubles.  
(B) The pressure in the container increases but does not double.  
(C) The pressure in the container more than doubles.  
(D) The pressure in the container does not change.
13. Which of the following statements is true concerning real gases?
- (A) The observed pressure will be less than the ideal pressure, and the volume available for the gas particles is less than the volume of the container.  
(B) The observed pressure will be less than the ideal pressure, and the volume available for the gas particles is greater than the volume of the container.  
(C) The observed pressure will be greater than the ideal pressure, and the volume available for the gas particles is greater than the volume of the container.  
(D) The observed pressure will be greater than the ideal pressure, and the volume available for the gas particles is less than the volume of the container.

Use the following information to answer questions 14–16.

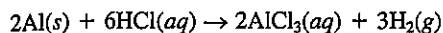


14. Indicate which of the above graphs represents  $PV(y)$  vs.  $V(x)$  for 1.0 mole of an ideal gas at constant  $T$ .  
15. Indicate which of the above graphs represents  $PV(y)$  vs.  $n(x)$  for an ideal gas at constant  $T$ .  
16. Indicate which of the above graphs represents gas density ( $y$ ) vs.  $T(x)$  for 1.0 mole of an ideal gas at constant  $P$ .

# AP Multiple-Choice Review Questions

Use the following information to answer questions 1 and 2.

Aluminum reacts with hydrochloric acid according to the following equation:



1. If a sample of 27.0 g of aluminum metal is added to 333 mL of 3.0 M hydrochloric acid, the volume of hydrogen gas produced at standard temperature and pressure is

(A) 2.80 L.  
(B) 5.60 L.  
(C) 11.2 L.  
(D) 22.4 L.

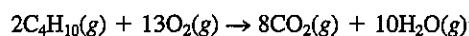
2. What is the approximate density of the hydrogen gas produced at STP?

(A) 0.1 g/L  
(B) 0.2 g/L  
(C) 0.3 g/L  
(D) 0.4 g/L

3. Given the following data,

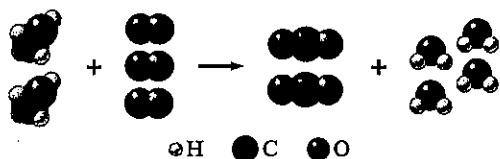
Substance	$\Delta H_f^\circ$ (kJ/mol)
$\text{CO}_2(g)$	-393.5
$\text{H}_2\text{O}(g)$	-285.8
$\text{C}_4\text{H}_{10}(g)$	-124.7

calculate the  $\Delta H_{rxn}^\circ$  for the following reaction.



(A) -6255.4 kJ  
(B) -5756.6 kJ  
(C) -40.6 kJ  
(D) 539.4 kJ

4. Consider the reaction shown below:

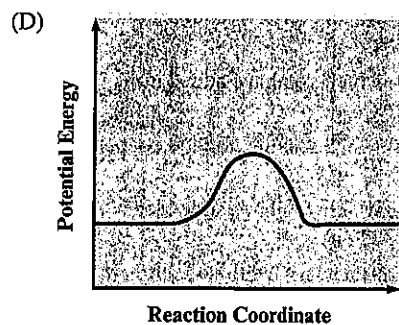
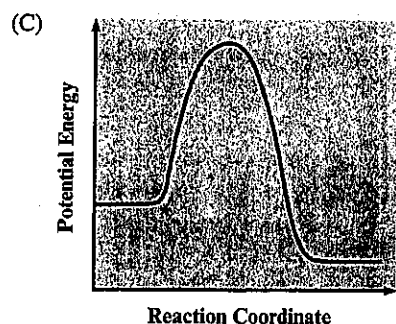
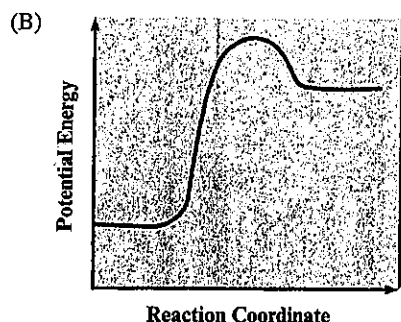
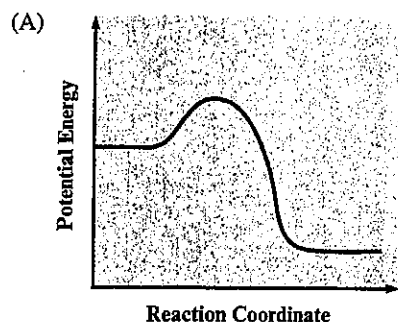


Given the following information, calculate  $\Delta H_{rxn}^\circ$  for the reaction represented above, where each molecule represents 1 mole of that substance. Assume that all states are those that are listed below.

Substance	$\Delta H_f^\circ$ (kJ/mol)
$\text{CO}_2(g)$	-393.5
$\text{H}_2\text{O}(g)$	-285.8
$\text{CH}_3\text{OH}(g)$	-201.0

(A) -2332.2 kJ  
(B) -1528.2 kJ  
(C) -478.3 kJ  
(D) 45.8 kJ

5. Which of the following graphs describes a pathway of reaction that is exothermic with a high activation energy?

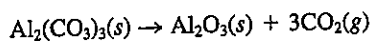


6. One cup of ice has a mass of approximately 250 g. The ice is at 0.0°C. How much heat is required to melt the ice and then warm the resulting water to 25.0°C? A table of useful information is provided.

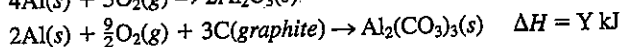
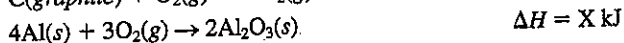
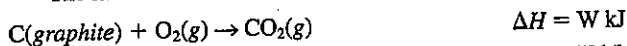
Heat of fusion of $\text{H}_2\text{O}(s)$	332 kJ/kg
Specific heat of $\text{H}_2\text{O}(l)$	4.18 J/°C · g

(A) 25 kJ  
(B) 58 kJ  
(C) 83 kJ  
(D) 110 kJ

7. A 20.-g sample of metal at  $110.^{\circ}\text{C}$  is placed into 30. g of kerosene at  $35.^{\circ}\text{C}$ . The final temperature of both the kerosene and the metal is  $60.^{\circ}\text{C}$ . If the specific heat of kerosene is  $2.0 \text{ J}^{\circ}\text{C}^{-1} \cdot \text{g}$ , what is the specific heat of the metal?
- (A)  $1.0 \text{ J}^{\circ}\text{C}^{-1} \cdot \text{g}$   
 (B)  $1.5 \text{ J}^{\circ}\text{C}^{-1} \cdot \text{g}$   
 (C)  $2.0 \text{ J}^{\circ}\text{C}^{-1} \cdot \text{g}$   
 (D)  $2.5 \text{ J}^{\circ}\text{C}^{-1} \cdot \text{g}$
8. Calculate the enthalpy change for the following reaction given the information below.



The information available to you is:

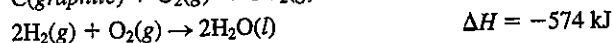
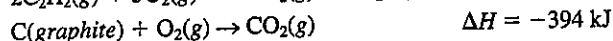
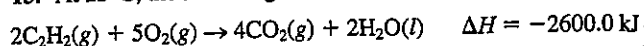


- (A)  $W + X - Y$   
 (B)  $3W + X - Y$   
 (C)  $3W + \frac{1}{2}X + Y$   
 (D)  $3W + \frac{1}{2}X - Y$
9. In which of the following isothermal expansions of an ideal gas is the work done by the system the largest? Assume the temperature is the same for all choices.
- (A) from 1 to 5 L against an opposing pressure of  $\frac{1}{2}$  atm  
 (B) from 1 to 5 L against an opposing pressure of 1 atm  
 (C) from 1 to 5 L against an opposing pressure of 3 atm  
 (D) from 1 to 10 L against an opposing pressure of 2 atm
10. Consider four 100.0-g samples of water, each in a separate beaker at  $25.0^{\circ}\text{C}$ . Into each beaker you drop 10.0 g of a different metal that has been heated to  $95.0^{\circ}\text{C}$ . Assuming no heat loss to the surroundings, which water sample will have the lowest final temperature?
- (A) the water to which you have added aluminum  
 ( $s = 0.89 \text{ J}^{\circ}\text{C}^{-1} \cdot \text{g}$ )  
 (B) the water to which you have added iron  
 ( $s = 0.45 \text{ J}^{\circ}\text{C}^{-1} \cdot \text{g}$ )  
 (C) the water to which you have added copper  
 ( $s = 0.20 \text{ J}^{\circ}\text{C}^{-1} \cdot \text{g}$ )  
 (D) the water to which you have added lead  
 ( $s = 0.14 \text{ J}^{\circ}\text{C}^{-1} \cdot \text{g}$ )
11. A student performs a neutralization reaction involving an acid and a base in an open polystyrene coffee-cup calorimeter. How would the calculated value of  $\Delta H$  differ from the actual value if there was significant heat loss to the surroundings?
- (A)  $\Delta H_{\text{calc}}$  would be negative, but more negative than the actual value.  
 (B)  $\Delta H_{\text{calc}}$  would be negative, but less negative than the actual value.  
 (C)  $\Delta H_{\text{calc}}$  would be positive, but more positive than the actual value.  
 (D)  $\Delta H_{\text{calc}}$  would be positive, but less positive than the actual value.

12. Which of the following is endothermic?

- (A) Water freezes to form ice.  
 (B) Steam condenses on a bathroom mirror.  
 (C) Ice cream melts.  
 (D) Coffee cools as it sits.

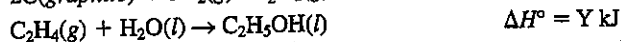
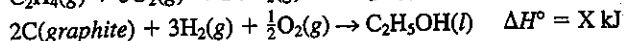
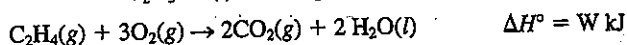
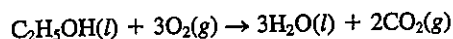
13. At  $25^{\circ}\text{C}$ , the following heats of reaction are known:



At the same temperature, calculate  $\Delta H$  for the reaction  $2\text{C}(\text{graphite}) + \text{H}_2(\text{l}) \rightarrow \text{C}_2\text{H}_2(\text{g})$ .

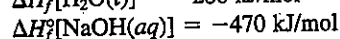
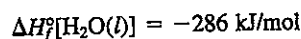
- (A)  $-2422 \text{ kJ}$   
 (B)  $-225 \text{ kJ}$   
 (C)  $225 \text{ kJ}$   
 (D)  $2422 \text{ kJ}$

14. Using Hess's law and the equations below find  $\Delta H^{\circ}$  at  $25^{\circ}\text{C}$  for the oxidation of  $\text{C}_2\text{H}_5\text{OH}(\text{l})$ .



- (A)  $W - Y$   
 (B)  $X - 2Y$   
 (C)  $X + 2W + Y$   
 (D)  $2X - W + Y$

15. A popular chemistry demonstration is to drop a piece of sodium metal into water. The products are sodium hydroxide and hydrogen gas. Determine  $\Delta H_{\text{rxn}}$  for this reaction for 1.00 mole of hydrogen gas being produced, given

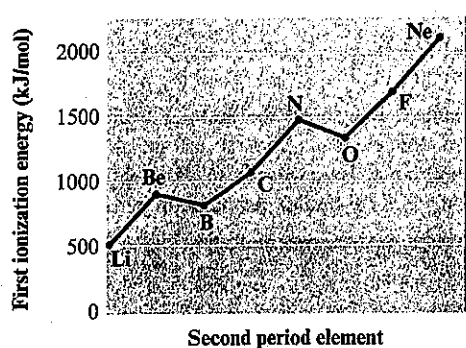


- (A)  $-368 \text{ kJ}$   
 (B)  $-184 \text{ kJ}$   
 (C)  $184 \text{ kJ}$   
 (D)  $368 \text{ kJ}$

## AP Multiple-Choice Review Questions

1. The first ionization energy of magnesium is 738 kJ/mol. A good estimate for the second ionization energy of magnesium is
- 370 kJ/mol
  - 735 kJ/mol
  - 1450 kJ/mol
  - 6900 kJ/mol

Use the following graph to answer questions 2–4.






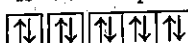
2. Which of the following is the *reason* that ionization energy generally increases from left to right across the first period of the periodic table?
- As the atomic number increases, the electrons are harder to remove.
  - Ionization energy increases as the atomic number increases in a period.
  - As the atomic number increases, more electrons are added to the atoms, thus increasing the electron–electron repulsions.
  - As the atomic number increases, more protons in the nucleus cause an increase in the effective nuclear charge, making it harder to remove the electrons.
3. What is the best explanation for the decrease in first ionization energy moving from Be to B?
- Moving from Be to B, more electrons are added to the atoms, thus increasing the electron–electron repulsions.
  - Moving from Be to B, more protons in the nucleus attract the valence electrons, making it harder to remove the electrons.
  - The electrons in Be are being removed from a full subshell, which is more stable than the half-filled subshell in B.
  - The electrons in Be are located in the 2s subshell, which is closer to the nucleus and thus harder to remove than the 2p electrons in B.

4. What is the best explanation for the decrease in first ionization energy moving from N to O?
- The oxygen atom is smaller, thus making it easier to remove the electrons compared with N.
  - The electrons in N are being removed from a half-full subshell, which is more stable than the partially filled subshell in O.
  - The electrons in N occupy the 2p orbitals singularly, whereas the electrons in one of the 2p orbitals of O are paired, thus increasing the electron–electron repulsions.
  - Moving from N to O, there are more protons in the nucleus, thus increasing the effective nuclear charge ( $Z_{\text{eff}}$ ), causing a greater amount of attraction for the valence electrons and making it harder to remove the electrons.
5. The table shows the first ionization energies of element X in kJ/mol.

First ionization energy (kJ/mol)	Second ionization energy (kJ/mol)	Third ionization energy (kJ/mol)
738	1450	7730

What is the most likely formula of the compound between element X and Y, where Y is a halogen?

- XY
  - XY<sub>2</sub>
  - XY<sub>3</sub>
  - X<sub>3</sub>Y
6. Which diagram shows an excited state?
- $1s \uparrow$
  - $1s \uparrow \quad 2s \uparrow$
  - $1s \uparrow \downarrow \quad 2s \uparrow \downarrow \quad 2p \uparrow \uparrow \uparrow$
  - $1s \uparrow \downarrow \quad 2s \uparrow \downarrow \quad 2p \uparrow \downarrow \uparrow \downarrow$
7. What is the electron configuration for Zn<sup>2+</sup>?
- 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>3d<sup>8</sup>
  - 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>3d<sup>10</sup>
  - 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>3d<sup>8</sup>4s<sup>2</sup>
  - 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>3d<sup>10</sup>4s<sup>2</sup>
8. Which of the following electron configurations shows the ground state of an ion of a halogen?
- 1s<sup>2</sup>2s<sup>2</sup>2p<sup>5</sup>3s<sup>2</sup>3p<sup>5</sup>
  - 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>
  - 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>3d<sup>5</sup>
  - 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>2d<sup>10</sup>3s<sup>2</sup>3p<sup>6</sup>

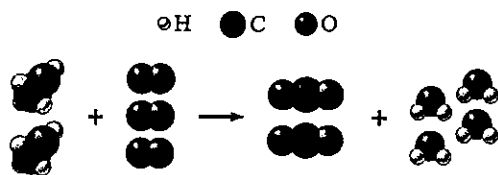
9. When placed in order of increasing atomic radius, what is the correct order for the elements Al, Ca, and Mg?
- (A) Al, Mg, Ca  
(B) Mg, Al, Ca  
(C) Ca, Al, Mg  
(D) Ca, Mg, Al
10. Which of the following electron configurations shows a violation of Hund's rule?
- (A)  $1s$   

- (B)  $1s \ 2s$   

- (C)  $1s \ 2s \ 2p$   

- (D)  $1s \ 2s \ 2p$   

11. The reactivity of the alkali metals increases going down the group. Which is the correct explanation for this trend?
- (A) The ionization energy decreases as you move down the group, thus it requires less energy to remove the valence electron and results in greater reactivity.  
(B) The greater nuclear charge as you move down the group results in a greater ability to attract electrons to the atom, thus making them more reactive.  
(C) As you move down the group, the nucleus's stability decreases, thus causing an increase in the number of radioactive isotopes, hence an increase in the reactivity of the alkali metals.  
(D) The greater mass as you move down the group causes an increase in the kinetic energy for any given molecular velocity. The increase in kinetic energy accounts for the increase in reactivity.
12. In which of the following electron transitions for a hydrogen atom does the light emitted have the longest wavelength?
- (A)  $n = 5$  to  $n = 2$   
(B)  $n = 4$  to  $n = 3$   
(C)  $n = 3$  to  $n = 1$   
(D)  $n = 2$  to  $n = 1$
13. An element X has the ground-state valence electron configuration of  $ns^2np^5$ . The formula for the compound composed of element X and nitrogen is most likely
- (A) NX  
(B)  $NX_2$   
(C)  $NX_3$   
(D)  $NX_5$
14. When placed in order of increasing ionization energy, what is the correct order for the species O,  $O^+$ , and  $O^-$ ?
- (A) O,  $O^+$ ,  $O^-$   
(B) O,  $O^-$ ,  $O^+$   
(C)  $O^+$ , O,  $O^-$   
(D)  $O^-$ , O,  $O^+$
15. The table below shows the first eight ionization energies for four random elements from the second and third periods of the periodic table. Based on these data, which elements would most likely have similar chemical properties?

	W	X	Y	Z
First	1,314	1,000	578	496
Second	3,388	2,252	1,817	4,562
Third	5,301	3,357	2,745	6,910
Fourth	7,469	4,556	11,577	9,543
Fifth	10,990	7,004	14,842	13,354
Sixth	13,327	8,496	18,379	16,613
Seventh	71,330	27,107	23,326	20,117
Eighth	84,078	31,719	27,465	25,496

- (A) W and X  
(B) W and Y  
(C) X and Z  
(D) Y and Z

## AP Multiple-Choice Review Questions

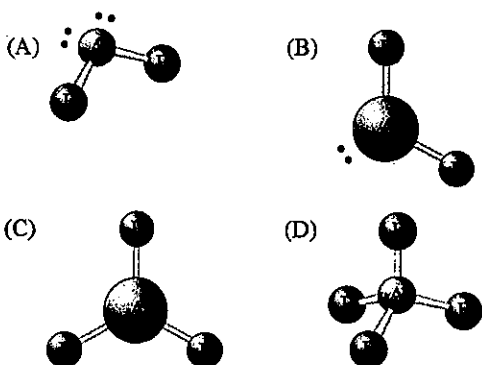
1. Consider the reaction shown below:



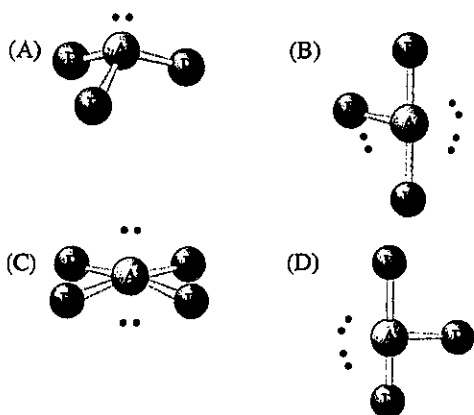
Type of Bond	Bond Energy (kJ/mol)
	500
	800
	475
	400

Determine  $\Delta H$  for the reaction represented above, where each molecule represents 1 mole of that substance.

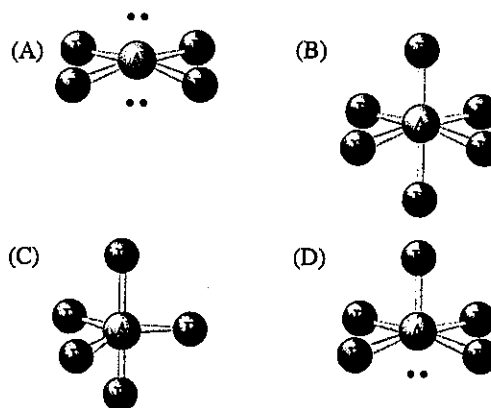
- (A)  $-2150 \text{ kJ}$   
 (B)  $-550 \text{ kJ}$   
 (C)  $100 \text{ kJ}$   
 (D)  $2175 \text{ kJ}$
2. Which of the following has a bent molecular geometry with a bond angle of approximately  $120^\circ$ ?



3. Which of the following is nonpolar?



4. Which diagram best represents the shape of the
- $\text{SF}_5^-$
- ion?



5. Which pair of elements is likely to produce a highly polar covalent bond?

- (A) Mg and O  
 (B) Li and F  
 (C) O and F  
 (D) C and F

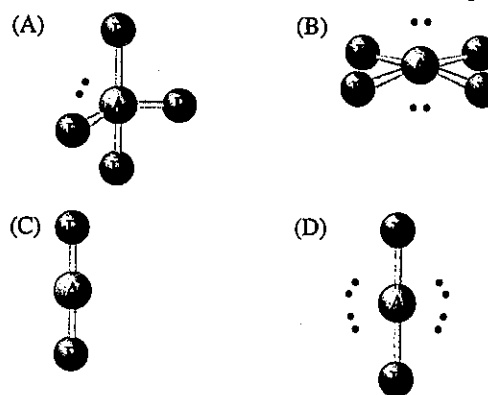
6. Which pair of elements is likely to produce a nearly nonpolar covalent bond?

- (A) Li and Rb  
 (B) Mg and O  
 (C) N and F  
 (D) Te and I

7. Which pair of elements is likely to produce an ionic bond?

- (A) O and F  
 (B) S and N  
 (C) Li and Cl  
 (D) Ca and Ba

8. Which molecule is likely to have a measurable dipole moment?

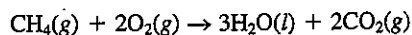


9. Of the most common ions of the third period elements Mg, Al, P, and S, which is the largest?

- (A) Mg  
 (B) Al  
 (C) P  
 (D) S



10. Determine
- $\Delta H$
- for the reaction of methane with oxygen.



C—H	400.
O=O	500.
C=O	800.
O—H	470.

- (A) -3420 kJ  
 (B) -880 kJ  
 (C) -430 kJ  
 (D) -370 kJ
11. Which of the following best explains the difference in the melting points of MgO (2852°C) and NaF (1819°C)?
- (A) There are greater Coulombic attractions in MgO due to the greater charges on the ions.  
 (B) Na is above Mg on the activity series of metals.  
 (C) F is more electronegative than O.  
 (D) Na is an alkali metal, and Mg is an alkaline earth metal. Alkali metals are more reactive than the alkaline earth metals.
12. The melting points of the compounds LiF, NaCl, KBr, and CsI exhibit the following trend:

Melting point order:  $\text{LiF} > \text{NaCl} > \text{KBr} > \text{CsI}$

Which of the following correctly explains this trend?

- (A) The increasing molar mass requires more energy to melt the substances.  
 (B) The greater radii of the larger ions results in smaller lattice energies, leading to lower melting points.  
 (C) Reactivity increases as you increase the atomic number in the alkali metals. The more reactive, the easier it is to lose electrons, hence a lower melting point.  
 (D) The melting point is directly proportional to the electronegative value for the halogen ions in the compound; there is more attraction for the electrons in the chemical bonds.

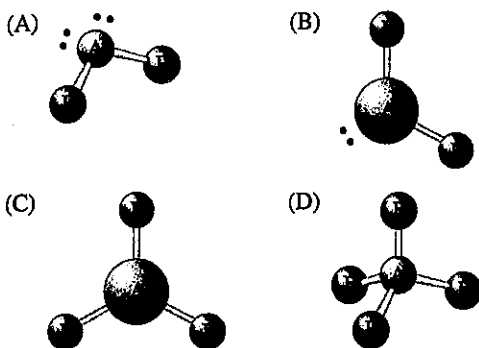
13. Use the following information to calculate the H—Cl bond energy.

$\text{H}_2(g) + \text{Cl}_2(g) \rightarrow 2\text{HCl}(g)$	-180
$\text{H}_2(g) \rightarrow 2\text{H}(g)$	430
$\text{Cl}_2(g) \rightarrow 2\text{Cl}(g)$	240

- (A) 325 kJ  
 (B) 425 kJ  
 (C) 490 kJ  
 (D) 950 kJ
14. Which of the following best describes  $\text{BF}_3$  and  $\text{NF}_3$ ? (Note: *Geometry* refers to the electron pair arrangement, and *shape* refers to the atom arrangement.)
- (A) They have the same geometry and different shapes.  
 (B) They have the same geometry and the same shape.  
 (C) They have different geometry and different shapes.  
 (D) They have different geometry and the same shape.
15. Which of the following correctly ranks the following species from smallest to largest ionic radius?
- (A)  $\text{Cl}^-$ ,  $\text{S}^{2-}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$   
 (B)  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{S}^{2-}$   
 (C)  $\text{S}^{2-}$ ,  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$   
 (D)  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{S}^{2-}$

## AP Multiple-Choice Review Questions

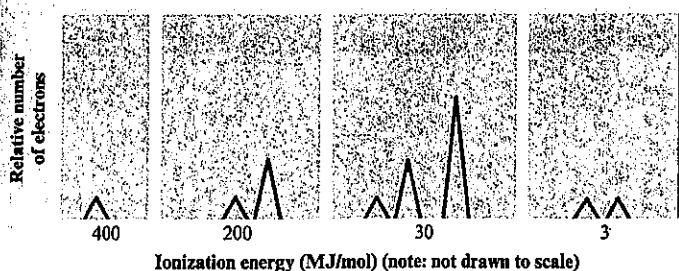
1. Which of the following has  $sp^3$  hybridization and is bent?



2. The expected electron configuration for copper should be  $[\text{Ar}]4s^23d^9$ . However, copper's electron configuration is  $[\text{Ar}]4s^13d^{10}$ . Which of the following would provide experimental evidence of copper's exception to the normal electron configuration?

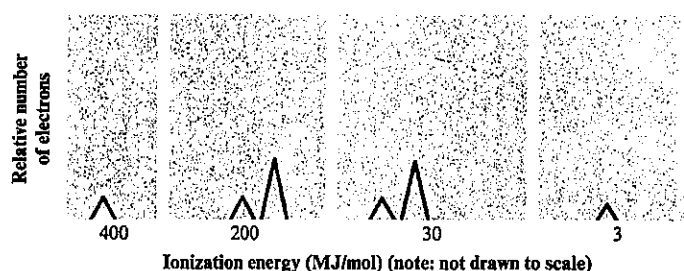
- (A) The mass spectrum of copper shows the different isotopes of copper.  
 (B) Copper ions in solution have color, which indicates that there are unpaired  $d$  orbital electrons.  
 (C) The photoelectron spectroscopy spectrum for copper shows the relative number of electrons in each orbit.  
 (D) Copper has the ability to form cations of plus one and plus two, whereas the other transition elements generally form cations of plus two and plus three.

3. Identify the element whose photoelectron spectrum is shown below.

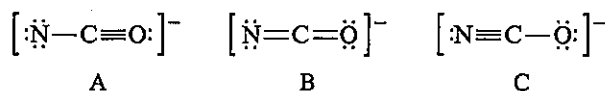


- (A) O  
 (B) Ca  
 (C) Ti  
 (D) Ge

4. Identify the element whose photoelectron spectrum is shown below.



- (A) N  
 (B) K  
 (C) Ca  
 (D) Sc
5. In a molecule in which the central atom exhibits  $sp^3$  hybrid orbitals, the electron pairs are directed toward the corners of a  
 (A) tetrahedron  
 (B) trigonal pyramid  
 (C) trigonal bipyramid  
 (D) square-based pyramid
6. Of  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{CO}_2$ , and  $\text{CO}$ , which one has the shortest C—O bond length?  
 (A)  $\text{HCO}_3^-$   
 (B)  $\text{CO}_3^{2-}$   
 (C)  $\text{CO}_2$   
 (D)  $\text{CO}$
7. Which ion listed has no resonance structures and exactly two pi ( $\pi$ ) bonds?  
 (A)  $\text{CN}^-$   
 (B)  $\text{O}_3^-$   
 (C)  $\text{OH}^-$   
 (D)  $\text{CO}_3^{2-}$
8. In a molecule in which the central atom exhibits  $sp^2$  hybrid orbitals, the arrangement of electron pairs is  
 (A) linear  
 (B) tetrahedral  
 (C) trigonal planar  
 (D) trigonal bipyramidal
9. The cyanate ion has three possible Lewis structures. Based on formal charges, which Lewis structure is the dominant structure, that is, the structure that best represents the cyanate ion?



- (A) Diagram A best represents the cyanate ion.  
 (B) Diagram B best represents the cyanate ion.  
 (C) Diagram C best represents the cyanate ion.  
 (D) Due to resonance, all three diagrams best represent the cyanate ion.

10. Which of the following is ionic and contains both sigma ( $\sigma$ ) and pi ( $\pi$ ) bonds?

- (A)  $\text{NO}_2$
- (B)  $\text{KCN}$
- (C)  $\text{C}_2\text{H}_4$
- (D)  $\text{NaOH}$

11. How many of the following molecules have two pi ( $\pi$ ) bonds?

$\text{HCN}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{OCl}_2$

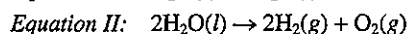
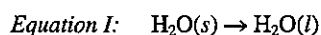
- (A) 0
- (B) 1
- (C) 2
- (D) 3

## AP Multiple-Choice Review Questions

1. The boiling points of hydrogen chloride and hydrogen bromide are given in the table below. Based on periodicity and intermolecular forces, which of the other two hydrogen halides would have a boiling point that is higher than that of HBr?

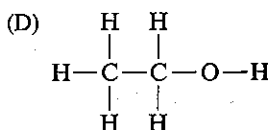
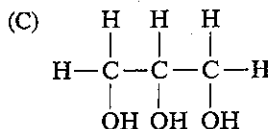
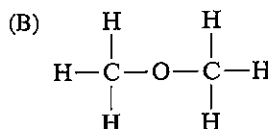
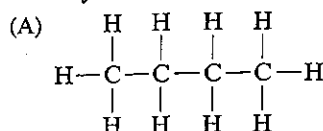
	HCl	HBr	HI	HF
Boiling point (°C)	-85°C	-66°C	?	?

- (A) HI only  
 (B) HF only  
 (C) HI and HF  
 (D) Neither HI nor HF
2. A correct representation of an ionic solid could be described as having
- (A) mobile valence electrons shared between positive metal ions  
 (B) positive and negative ions in fixed positions in a framework  
 (C) electrons and positive metal ions in fixed positions in a framework  
 (D) metallic and nonmetallic atoms bonded covalently in a three-dimensional pattern
3. Ionic solids are not able to conduct electricity in the solid phase but are able to conduct electricity when dissolved in water. This can best be explained by the fact that the ions
- (A) release free electrons when dissolved in water  
 (B) form molecules that conduct electricity when dissolved in water  
 (C) are in fixed positions in the solid phase, whereas they are free to move in solution  
 (D) are not able to conduct electricity themselves, but water molecules can conduct electricity
4. Which statement correctly describes the changes occurring in the two equations shown below?



- (A) Equation I represents a physical change because only intermolecular bonds are broken, whereas Equation II represents a chemical change because intramolecular bonds are broken.  
 (B) Equation I represents a physical change because only intramolecular bonds are broken, whereas Equation II represents a chemical change because intermolecular bonds are broken.  
 (C) Equation I represents a chemical change because only intermolecular bonds are broken, whereas Equation II represents a physical change because intramolecular bonds are broken.  
 (D) Equation I represents a chemical change because only intramolecular bonds are broken, whereas Equation II represents a physical change because intermolecular bonds are broken.

5. Based on molecular structure and intermolecular forces, which of these substances would you predict to have the greatest viscosity?

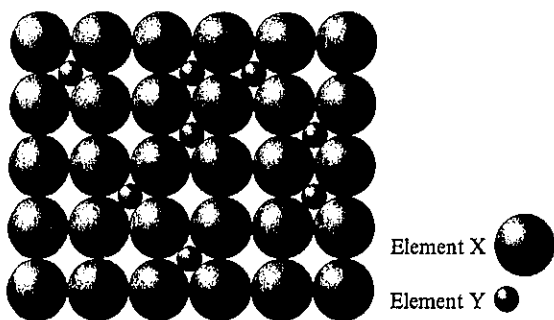


6. The physical properties of four unknown pure substances were determined in a laboratory. Based on the information given in the table below, which correctly identifies the type of element or compound?

	Physical State	Boiling Point (°C)	Solubility in Water	Electrical Conductivity	Heat of Fusion (kJ/mol)
W	Solid	No	Soluble	Low	High
X	Solid	No	Insoluble	Low	Very high
Y	Liquid	No	Soluble	High	Low
Z	Solid	Yes	Insoluble	Low	High

- (A) W = covalent network; X = metallic; Y = molecular; Z = ionic  
 (B) W = molecular; X = covalent network; Y = ionic; Z = metallic  
 (C) W = metallic; X = ionic; Y = covalent network; Z = molecular  
 (D) W = ionic; X = covalent network; Y = molecular; Z = metallic
7. In which of the following groups are the noble gases arranged correctly in order of increasing boiling point?
- (A) He, Ne, Kr, Xe  
 (B) Ne, He, Kr, Xe  
 (C) Kr, Xe, Ne, He  
 (D) Xe, Kr, Ne, He
8. A 10-lane Olympic-sized swimming pool contains  $2.5 \times 10^6$  kg of water. If the water is at 0°C, how many kilojoules of energy must be removed to freeze the water in this pool?  $\Delta H_{\text{fus}}$  for  $\text{H}_2\text{O} = 334 \text{ J/g}$
- (A)  $7.5 \times 10^3 \text{ kJ}$   
 (B)  $8.4 \times 10^5 \text{ kJ}$   
 (C)  $7.5 \times 10^6 \text{ kJ}$   
 (D)  $8.4 \times 10^8 \text{ kJ}$

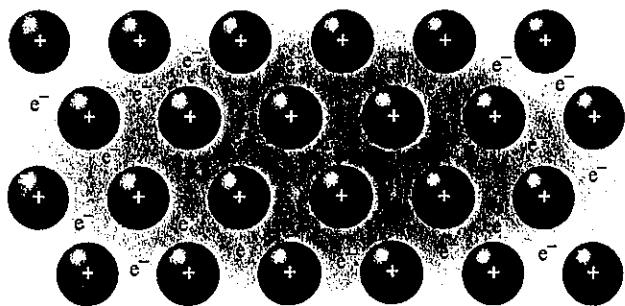
9. An example of an alloy is shown in the diagram below. Compared with the pure metal X, how would you expect the properties of the alloy to vary?



- (A) The alloy has higher malleability and higher density.  
 (B) The alloy has lower malleability and lower density.  
 (C) The alloy has higher malleability and lower density.  
 (D) The alloy has lower malleability and higher density.
10. Which best explains why an aluminum can may be crushed without it breaking into pieces?



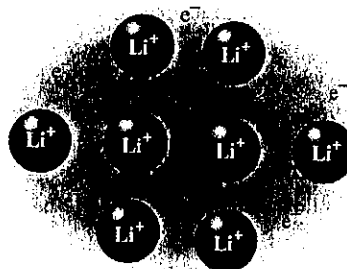
- (A) Aluminum has ionic bonds that are not easily broken.  
 (B) Aluminum has covalent bonds that are not easily broken.  
 (C) Aluminum has localized valence electrons with directional bonding.  
 (D) Aluminum has delocalized valence electrons with nondirectional bonding.
11. A sample of an unknown material consists of positive ions surrounded by delocalized valence electrons. Which properties are likely for this material?
- (A) poor conductor of electricity, brittle, volatile  
 (B) good conductor of electricity, easily deformed, nonvolatile  
 (C) poor conductor of electricity, easily deformed, volatile  
 (D) good conductor of electricity, brittle, nonvolatile
12. A representation of the bonding in solid silver is shown below.



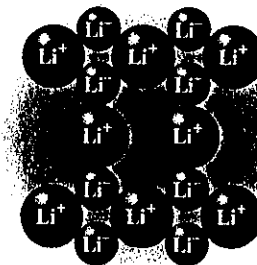
This representation best shows which of the following?

- (A) Each silver atom has one valence electron that is tightly bound to the atom, resulting in a rigid, hard material.  
 (B) Each silver atom has one valence electron that is found in the interstitial holes of the silver crystal structure, making it behave as an alloy.  
 (C) Each silver atom has one valence electron that is free to move throughout the piece of metal, allowing silver to conduct electricity.  
 (D) Each silver atom loses an electron to form a silver cation. This makes the silver very soluble.
13. Which best represents the structure and bonding in solid lithium?

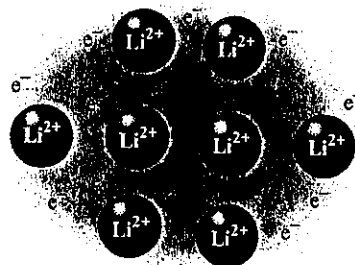
(A)



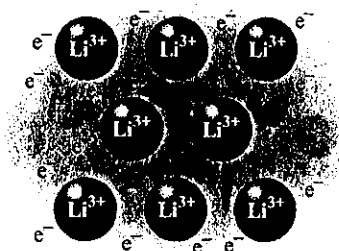
(B)



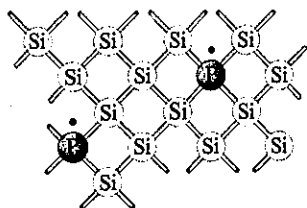
(C)



(D)



14. Doping of silicon is achieved by the substitution of a different element for some of the silicon atoms. What type of semiconductor is shown below?

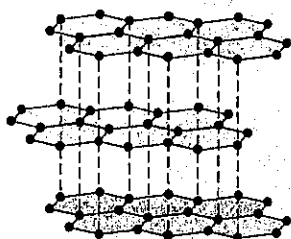


- (A) It is a p-type semiconductor because the phosphorus atoms have one more electron than the silicon atoms.  
 (B) It is an n-type semiconductor because the phosphorus atoms have one more electron than the silicon atoms.  
 (C) It is an n-type semiconductor because phosphorus is a nonmetal, whereas silicon is a metalloid.  
 (D) It is a p-type semiconductor because phosphorus was substituted for silicon, rather than nitrogen being substituted for silicon.
15. An unknown solid substance was found to have the following properties:

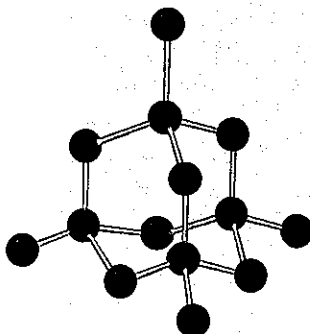
1. Extremely high melting point
2. Conducts electricity in solid form
3. Breaks apart easily

Which of these compounds could be this unknown substance?

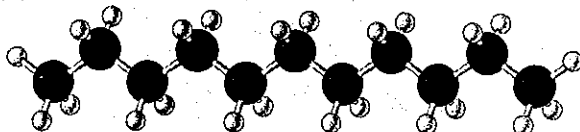
(A)



(B)



(C)

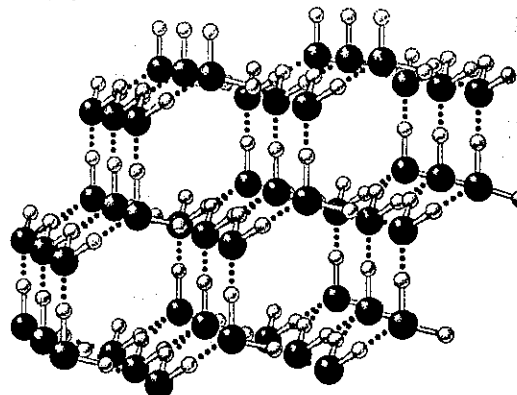


(D)

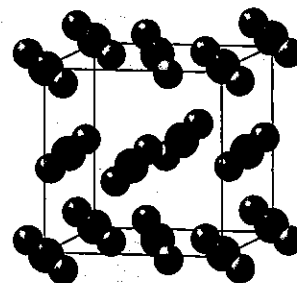


16. Which of these would best show the structure of solid carbon dioxide (dry ice)?

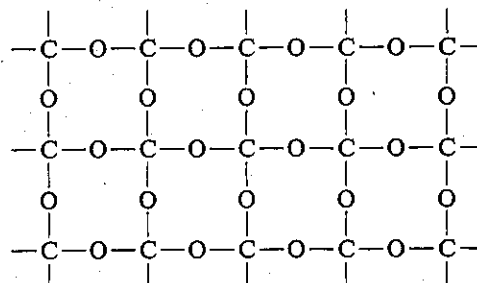
(A)



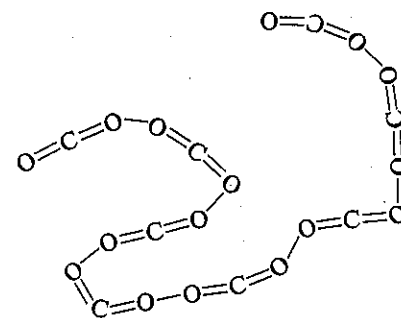
(B)



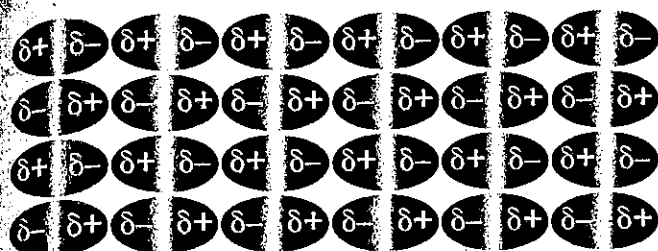
(C)



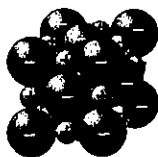
(D)



17. Which of the following is true for a solid with a structure as shown in the diagram below?



- (A) It is an atomic solid and consists of atoms with electrostatic attractions.
- (B) It is an ionic solid and consists of ions held together by electrostatic attractions.
- (C) It is a molecular solid and consists of polar molecules with dipole-dipole attractions.
- (D) It is a molecular solid and consists of nonpolar molecules with intermolecular forces.
18. Which of these correctly matches the molecular compound with the most important force between molecules of the same substance?
- (A) ammonia: hydrogen bonding
- (B) hydrogen cyanide: ionic bonding
- (C) propane ( $C_3H_8$ ): dipole-dipole attractions
- (D) hydrogen sulfide: London dispersion forces
19. What properties would a compound like the one pictured below be likely to have in its pure, solid form?



- (A) high vapor pressure, low melting point, nonconductor of electricity
- (B) high vapor pressure, high melting point, good conductor of electricity
- (C) low vapor pressure, high melting point, good conductor of electricity
- (D) low vapor pressure, high melting point, nonconductor of electricity

20. Which of these statements provides an accurate comparison of the general properties of solids and liquids?

- (A) In a solid, particles are slightly closer together, have greater interparticle attractions, and have lower particle motion compared with a liquid.
- (B) In a solid, particles are slightly further apart, have weaker interparticle attractions, and have lower particle motion compared with a liquid.
- (C) In a solid, particles are slightly closer together, have weaker interparticle attractions, and have greater particle motion compared with a liquid.
- (D) In a solid, particles are slightly further apart, have weaker interparticle attractions, and have greater particle motion compared with a liquid.
21. Silicon dioxide,  $SiO_2$ , is a covalent network solid with each silicon atom bonded to four oxygen atoms, forming a large network of  $SiO_4$  tetrahedra of great strength. Which of these other compounds would you predict to have similar properties?
- (A)  $MgO$
- (B)  $CO_2$
- (C)  $SO_2$
- (D)  $GeO_2$

## AP Multiple-Choice Review Questions

1. Which of the following conditions most favors the process of dissolution?

## Strength of Attraction between Different Substances

	Solvent-Solvent	Solvent-Solute	Solute-Solute
(A)	Weak	Weak	Weak
(B)	Weaker	Weaker	Stronger
(C)	Weaker	Stronger	Weaker
(D)	Stronger	Weaker	Weaker

- (A) Weak      Weak      Weak  
(B) Weaker      Weaker      Stronger  
(C) Weaker      Stronger      Weaker  
(D) Stronger      Weaker      Weaker
2. Determine the molarity of a solution that is made by dissolving 20.0 g of ammonium nitrate,  $\text{NH}_4\text{NO}_3$ , in enough water to make 250.0 mL of solution.
- (A) 0.250 M  
(B) 1.00 M  
(C) 2.00 M  
(D) 4.00 M
3. Nonpolar solutes dissolve more readily in nonpolar solvents than polar solvents because
- (A) the induced dipole of the solute molecule creates an induced dipole in the solvent molecule and London dispersion forces occur.  
(B) the induced dipole of the solute molecule creates a permanent dipole in the solvent molecule and London dispersion forces occur.  
(C) the permanent dipole of the solute molecule creates an induced dipole in the solvent molecule and London dispersion forces occur.  
(D) the permanent dipole of the solute molecule creates a permanent dipole in the solvent and London dispersion forces occur.
4. Predict what effect increasing the charge of the metal ion has on the solubility in water of KCl compared with  $\text{CaCl}_2$ .
- (A) The solubility of KCl is less than that of  $\text{CaCl}_2$  due to stronger Coulombic forces in the KCl.  
(B) The solubility of KCl is less than that of  $\text{CaCl}_2$  due to weaker Coulombic forces in the KCl.  
(C) The solubility of KCl is greater than that of  $\text{CaCl}_2$  due to stronger Coulombic forces in the KCl.  
(D) The solubility of KCl is greater than that of  $\text{CaCl}_2$  due to weaker Coulombic forces in the KCl.
5. Which of the following is the best explanation of how the ions in KCl interact with a polar solvent in the process of dissolution?
- (A) The  $\text{K}^+$  ions are attracted to the negative end of the polar solvent, and the  $\text{Cl}^-$  ions are attracted to the positive end.  
(B) The  $\text{K}^+$  ions are attracted to the positive end of the polar solvent, and the  $\text{Cl}^-$  ions are attracted to the negative end.  
(C) Both the  $\text{K}^+$  and the  $\text{Cl}^-$  ions are attracted to the negative end of the polar solvent.  
(D) Both the  $\text{K}^+$  and the  $\text{Cl}^-$  ions are attracted to the positive end of the polar solvent.

6. Iodine crystals dissolve in hexane more readily than in water. However, if the iodine crystals are left in the water for an extended time period, they will dissolve at the interface. This can best be explained because

- (A) iodine, although nonpolar in nature, has permanent dipoles that can interact with the polar water molecules.  
(B) iodine, although nonpolar in nature, has momentary dipoles that can then interact with the polar water molecules.  
(C) iodine, although nonpolar in nature, has a large molar mass, which allows it to interact with the polar water molecules.  
(D) iodine, although nonpolar in nature, has a relatively low melting point, which allows it to interact with the polar water molecules.

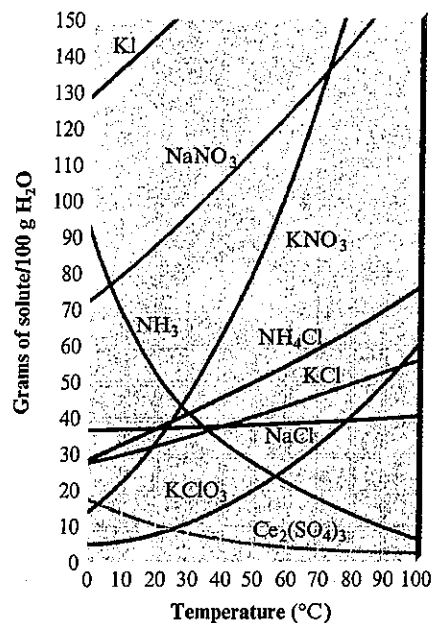
7. Arrange the hydroxides from least soluble to most soluble based on their relative  $K_{sp}$  values.

KOH	$K_{sp} = \text{very large}$
$\text{Ca}(\text{OH})_2$	$K_{sp} = 5.0 \times 10^{-6}$
$\text{Al}(\text{OH})_3$	$K_{sp} = 3.0 \times 10^{-34}$

- (A) KOH,  $\text{Al}(\text{OH})_3$ ,  $\text{Ca}(\text{OH})_2$   
(B) KOH,  $\text{Ca}(\text{OH})_2$ ,  $\text{Al}(\text{OH})_3$   
(C)  $\text{Al}(\text{OH})_3$ ,  $\text{Ca}(\text{OH})_2$ , KOH  
(D)  $\text{Ca}(\text{OH})_2$ ,  $\text{Al}(\text{OH})_3$ , KOH
8. A student attempted to dissolve a liquid ionic solute in a nonpolar solvent. The resulting mixture showed three distinct layers. This would be classified as a
- (A) chemical change because the ionic solute and nonpolar solvent did not mix.  
(B) physical change because the ionic solute and nonpolar solvent did not mix.  
(C) chemical change because three distinct layers were formed.  
(D) physical change because three distinct layers were formed.
9. Which compound would be expected to be the most soluble in water?
- (A)  $\text{C}_6\text{H}_6$   
(B)  $\text{CHBr}_3$   
(C)  $\text{C}_6\text{H}_{14}$   
(D)  $\text{CH}_3\text{NH}_2$



10. A student dissolved 30 g of an unknown compound in 50 g of water at 39°C. What is the unknown compound?



- (A) Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>  
(B) KCl  
(C) NH<sub>4</sub>Cl  
(D) KNO<sub>3</sub>

## AP Multiple-Choice Review Questions

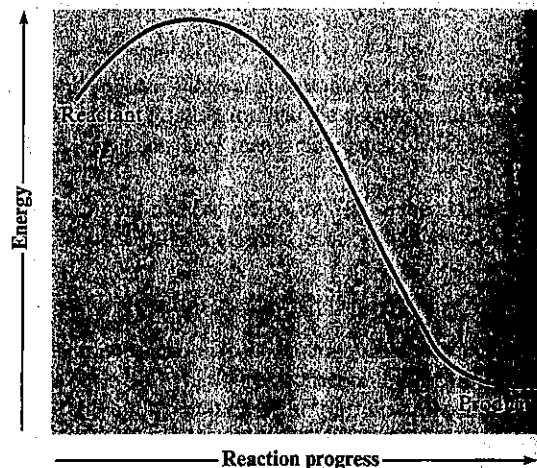
1. Magnesium reacts with hydrochloric acid to produce hydrogen gas. An experiment was set up to determine the rate of production of the hydrogen gas by measuring its change in volume over the first 60 seconds of the reaction. Magnesium ribbon was cut into squares of  $0.5\text{ cm}^2$  and  $1.0\text{ cm}^2$ . The volume of hydrochloric acid solution and the total mass of magnesium were held constant in each trial. Which set of conditions would produce the highest rate of production of hydrogen gas?
- (A)  $1\text{ M HCl}$ ,  $0.5\text{-cm}^2$  pieces of magnesium  
 (B)  $1\text{ M HCl}$ ,  $1.0\text{-cm}^2$  pieces of magnesium  
 (C)  $3\text{ M HCl}$ ,  $1.0\text{-cm}^2$  pieces of magnesium  
 (D)  $3\text{ M HCl}$ ,  $0.5\text{-cm}^2$  pieces of magnesium

Questions 2–4 refer to the following:

Given the reaction:  $\text{A} + 2\text{B} \rightarrow \text{C}$

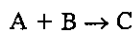
Trial	$[\text{A}]_0$ (mol/L)	$[\text{B}]_0$ (mol/L)	Rate of disappearance of B (mol/L s)
1	$1.2 \times 10^{-2}$	$1.2 \times 10^{-2}$	$1.8 \times 10^{-4}$
2	$1.2 \times 10^{-2}$	$2.4 \times 10^{-2}$	$7.2 \times 10^{-4}$
3	$2.4 \times 10^{-2}$	$1.2 \times 10^{-2}$	$3.6 \times 10^{-4}$

2. Based on the experimental data given in the table, what is the order of the reaction with respect to A?
- (A) zero  
 (B) first  
 (C) second  
 (D) third
3. Based on the experimental data given in the table, what is the order of the reaction with respect to B?
- (A) zero  
 (B) first  
 (C) second  
 (D) third
4. What is the rate of disappearance of B in trial 2?
- (A)  $2.4 \times 10^{-2}\text{ mol L}^{-1}\text{ s}^{-1}$   
 (B)  $1.4 \times 10^{-3}\text{ mol L}^{-1}\text{ s}^{-1}$   
 (C)  $3.6 \times 10^{-4}\text{ mol L}^{-1}\text{ s}^{-1}$   
 (D)  $7.2 \times 10^{-4}\text{ mol L}^{-1}\text{ s}^{-1}$
5. What is the value of  $k$  for a first-order reaction with a half-life of  $23.1\text{ s}$ ?
- (A)  $16.0\text{ s}^{-1}$   
 (B)  $16.0\text{ s}$   
 (C)  $0.0300\text{ s}^{-1}$   
 (D)  $0.0300\text{ s}$
6. In a chemical reaction that has first-order kinetics, which is true at constant temperature?
- (A) Half-life and  $k$  are both constant.  
 (B) Neither half-life nor  $k$  is constant.  
 (C) Half-life is constant, but  $k$  changes.  
 (D) Half-life changes, but  $k$  is constant.
7. The reaction  $\text{Q} + \text{R}_2 \rightarrow \text{R}_2\text{Q}$  is found to be first order in  $\text{R}_2$  and zero order in  $\text{Q}$ . Which of these mechanisms is most likely for this reaction?
- (A)  $\text{Q} + \text{R}_2 \rightarrow \text{R}_2\text{Q}$  (slow)  
 (B)  $2\text{Q} \rightarrow \text{Q}_2$  (slow)  
 $\text{Q}_2 + \text{R}_2 \rightarrow \text{R}_2\text{Q} + \text{Q}$  (fast)  
 (C)  $\text{Q} + \text{Z} \rightarrow \text{QZ}$  (slow)  
 $\text{QZ} + \text{R} \rightarrow \text{QR} + \text{Z}$  (fast)  
 $\text{QR} + \text{R} \rightarrow \text{R}_2\text{Q}$  (fast)  
 (D)  $\text{R}_2 \rightarrow 2\text{R}$  (slow)  
 $\text{R} + \text{Q} \rightarrow \text{RQ}$  (fast)  
 $\text{RQ} + \text{R} \rightarrow \text{R}_2\text{Q}$  (fast)
8. Which is true of the reaction diagram for an elementary reaction, such as the one shown?



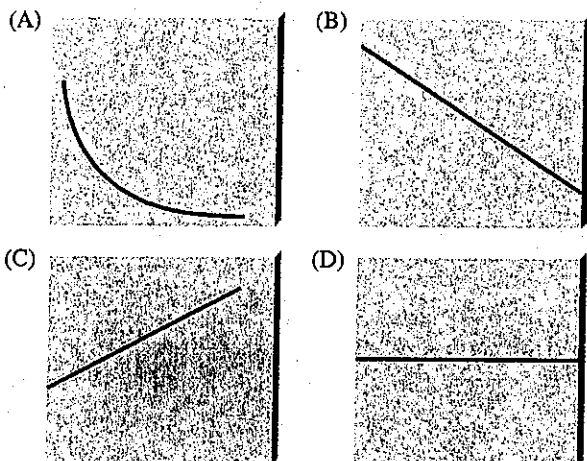
- (A) It consists of zero transition states and zero intermediates.  
 (B) It has one transition state and zero intermediates.  
 (C) It has one transition state and one intermediate.  
 (D) It has two transition states and two intermediates.
9. Which is a correct explanation for why the reaction rate increases with increasing temperature?
- (A) The reaction becomes more exothermic.  
 (B) The enthalpy change of the reaction increases.  
 (C) The activation energy of the reaction decreases.  
 (D) More of the colliding particles have the activation energy.
10. How would the net-ionic equation written for a catalyzed reaction differ from the net-ionic equation written for the same reaction without a catalyst?
- (A) The net-ionic equation would be different because an additional reactant is needed.  
 (B) The net-ionic equation would be different because the catalyst should be shown on both the reactant and product side.  
 (C) The net-ionic equation would be the same because the catalyst is a spectator ion and would be left out of a net ionic equation.  
 (D) The net-ionic equation would be the same because a catalyst is neither a reactant nor a product.

11. The following reaction was determined to be elementary:

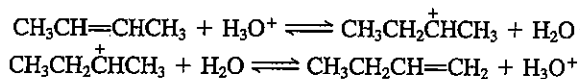


What is the overall order of the reaction and the units of the rate constant,  $k$ ?

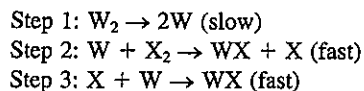
- (A) first order,  $\text{time}^{-1}$   
 (B) second order,  $\text{time}^{-1}$   
 (C) second order,  $L/(\text{mol} \times \text{time})$   
 (D) cannot determine the order and units of  $k$  without experimental data
12. The concentration of reactant versus time data were measured and plotted for a reaction with the rate law:  $\text{Rate} = k[A]^2$ . Which graph would result?



13. Many organic reactions, such as the two-step conversion of 2-butene to 1-butene as shown in the mechanism below, proceed at higher rates in the presence of an acid. What is the role of the  $\text{H}_3\text{O}^+$  in this mechanism?



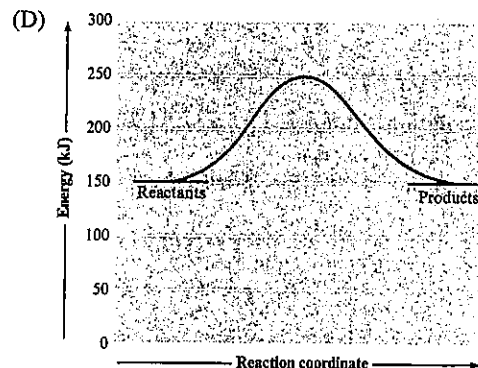
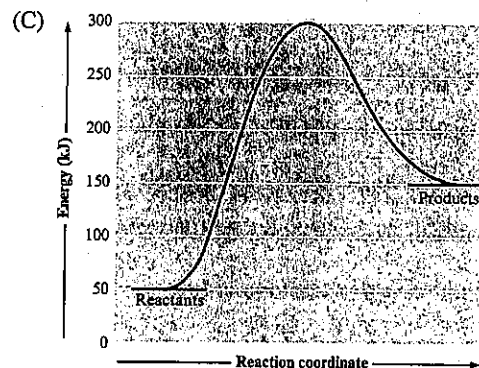
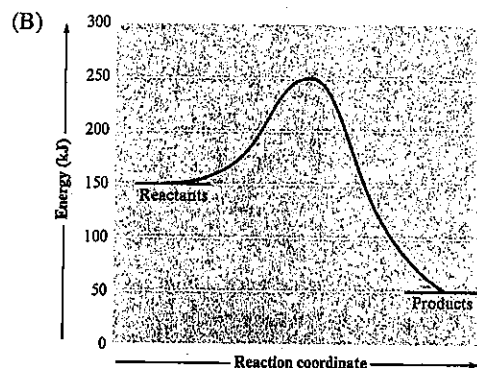
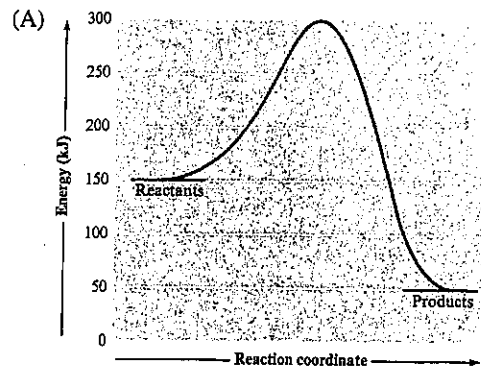
- (A) reactant  
 (B) catalyst  
 (C) inhibitor  
 (D) intermediate
14. A proposed mechanism for the reaction  $\text{W}_2 + \text{X}_2 \rightarrow 2\text{WX}$  is:



What rate law is supported by this mechanism?

- (A)  $\text{rate} = k[\text{W}_2]$   
 (B)  $\text{rate} = k[\text{W}][\text{X}_2]$   
 (C)  $\text{rate} = k[\text{W}_2][\text{X}_2]$   
 (D)  $\text{rate} = k[\text{W}_2]^{1/2}[\text{X}_2]$

15. Which energy profile represents the reaction that would occur at the lowest rate at a given temperature?



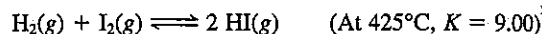
## AP Multiple-Choice Review Questions

- Consider the dissolution of an ionic salt in water. Which of the following statements best explains why this process is considered a physical change?
  - The ionic salt can be recovered by evaporation of the water.
  - The ionic salt can be recovered by solidification of the water.
  - Dissolution of an ionic salt is mostly a physical change, and all physical changes are reversible.
  - Dissolution of an ionic salt is mostly a chemical change, and all chemical changes are reversible.
- For the reaction  $A \rightleftharpoons B$ , for which value of  $K$  is the concentration of the reactants greater than the concentration of the products?
  - $K$  equals 0
  - $K$  equals 1
  - $K$  is less than 1
  - $K$  is greater than 1
- A solution with initial concentrations of  $6.00\text{ M Fe}^{3+}$  and  $10.0\text{ M SCN}^-$  is allowed to reach equilibrium. At equilibrium it is found that the concentration of  $\text{FeSCN}^{2+}$  is  $4.00\text{ M}$ . What are the equilibrium concentrations of the  $\text{Fe}^{3+}$  and  $\text{SCN}^-$ ?
 
$$\text{Fe}^{3+}(\text{aq}) + \text{SCN}^-(\text{aq}) \rightleftharpoons \text{FeSCN}^{2+}(\text{aq})$$
  - $[\text{Fe}^{3+}] = 4.00\text{ M}$ ;  $[\text{SCN}^-] = 4.00\text{ M}$
  - $[\text{Fe}^{3+}] = 2.00\text{ M}$ ;  $[\text{SCN}^-] = 6.00\text{ M}$
  - $[\text{Fe}^{3+}] = 6.00\text{ M}$ ;  $[\text{SCN}^-] = 2.00\text{ M}$
  - $[\text{Fe}^{3+}] = 2.00\text{ M}$ ;  $[\text{SCN}^-] = 2.00\text{ M}$
- Hydrogen gas at a pressure of  $9.0\text{ atm}$  is added to a container containing  $5.0\text{ atm}$  of iodine vapor. The resulting reaction is allowed to come to equilibrium, and it is found that the final pressure of iodine vapor is  $2.0\text{ atm}$ . What is the  $K_p$  value for the following reaction?
 
$$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$$
  - 0.25
  - 0.33
  - 3.0
  - 4.0
- Dinitrogen pentoxide is added to an evacuated rigid container at  $25^\circ\text{C}$ . Given that the initial pressure is  $1.00\text{ atm}$  and at equilibrium the pressure is  $0.500\text{ atm}$ , determine the final pressure in the reaction vessel at equilibrium.
 
$$2\text{N}_2\text{O}_5(\text{g}) \rightleftharpoons 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$$
  - $0.750\text{ atm}$
  - $1.00\text{ atm}$
  - $1.25\text{ atm}$
  - $1.75\text{ atm}$

- Determine the  $K_p$  for the following reaction if at equilibrium half of the initial  $\text{SO}_2$  reacted to form  $2.00\text{ atm}$  of  $\text{SO}_3$ . The initial partial pressure of  $\text{SO}_2$  and  $\text{O}_2$  were equal.
 
$$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$$
  - $0.250\text{ atm}$
  - $0.333\text{ atm}$
  - $0.500\text{ atm}$
  - $1.00\text{ atm}$
- An initial mixture of  $5.00\text{ M N}_2$  and  $5.00\text{ M H}_2$  is placed in a reaction vessel and allowed to come to equilibrium. The equilibrium concentration of the  $\text{NH}_3$  is determined to be  $2.00\text{ M}$ . Determine  $K$  for the reaction below.
 
$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$$
  - 0.125
  - 0.250
  - 0.500
  - 1.00

Questions 8–12 refer to the following:

Hydrogen gas, iodine vapor, and hydrogen iodide gas are added to an evacuated flask until the concentrations of  $\text{H}_2$  and  $\text{I}_2$  are both  $2.0\text{ M}$  and that of  $\text{HI}$  equals  $8.0\text{ M}$ .

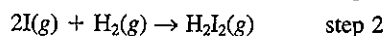
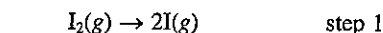


- Determine the value of  $Q$ .
  - 2.0
  - 4.0
  - 8.0
  - 16
- The reaction vessel is heated to  $675^\circ\text{C}$ , where the equilibrium concentration of the  $\text{HI}$  is determined to be  $6.0\text{ M}$ . What is the  $K$  value at  $675^\circ\text{C}$ ?
  - 6.0
  - 9.0
  - 24
  - 36
- Once the system reaches equilibrium at  $675^\circ\text{C}$ , additional  $\text{H}_2$  is added and the temperature is held constant. Which statement best describes how this affects the value of  $K$ ?
  - The value of  $K$  increases because the formation of products is favored.
  - The value of  $K$  decreases because the formation of reactants is favored.
  - The value of  $K$  remains unchanged because the temperature remained constant.
  - The value of  $K$  cannot be determined until the equilibrium concentrations are determined.

11. In a separate experiment to determine the rate law for this reaction, the data given in the table below were produced. Determine the rate law for this reaction.

Initial [H <sub>2</sub> ] (mol/L)	Initial [I <sub>2</sub> ] (mol/L)	Initial Rate (mol/L·min)
1.0	2.0	5.00
1.0	4.0	10.0
2.0	4.0	20.0

- (A) rate =  $k[\text{H}_2]$   
 (B) rate =  $k[\text{I}_2]$   
 (C) rate =  $k[\text{H}_2][\text{I}_2]$   
 (D) rate =  $k[\text{H}_2]^2[\text{I}_2]$
12. This reaction has been considered to occur as a single elementary, bimolecular mechanism. However, in a recent laboratory investigation, the mixture was irradiated with light. When the wavelength used supplied the energy needed to dissociate the iodine bond, this caused the reaction rate to increase significantly. This would support the following mechanism:



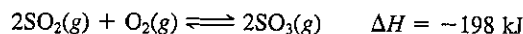
Which step in the mechanism would be the rate-determining step?

- (A) step 1  
 (B) step 2  
 (C) step 3  
 (D) cannot determine the rate-determining step without knowing the rate law
13. Consider the decomposition of potassium chlorate according to the reaction below. Which expression is needed to find the pressure of the O<sub>2</sub> if 61.2 g of the potassium chlorate (molar mass = 122.4 g/mol) decomposes in a rigid 2.5-L container at a temperature of 525°C? (Assume all the chlorate decomposed to form the products.)



- (A)  $\frac{(0.75)(0.0821)(525)}{2.5}$   
 (B)  $\frac{(0.75)(0.0821)(525 + 273)}{2.5}$   
 (C)  $(0.75)(0.0821)(525)(2.5)$   
 (D)  $\frac{(0.75)(0.0821)}{(2.5)(525 + 273)}$

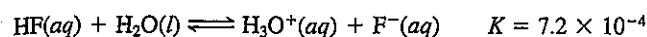
Questions 14 and 15 refer to the following reaction at equilibrium:



14. Which of the following occurs after the addition of O<sub>2</sub>?  
 (A) The rate of the forward reaction increases, and the value of  $K$  increases.  
 (B) The rate of the forward reaction decreases, and the value of  $K$  increases.  
 (C) The rate of the forward reaction decreases, and the value of  $K$  remains the same.  
 (D) The rate of the forward reaction increases, and the value of  $K$  remains the same.
15. Which of the following changes to the system at equilibrium would result in an increase in the concentration of O<sub>2</sub>?  
 (A) an increase in the concentration of SO<sub>2</sub> and an increase in the temperature  
 (B) an increase in the concentration of SO<sub>2</sub> and a decrease in the temperature  
 (C) an increase in the concentration of SO<sub>3</sub> and a decrease in the temperature  
 (D) an increase in the concentration of SO<sub>3</sub> and an increase in the temperature
16. It is found that the value of the reaction quotient is 12 for a given reaction, whereas the equilibrium constant is 8.0. Which statement best describes how the system will respond?  
 (A) Since  $Q > K$ , the forward reaction is favored and the equilibrium shifts to the right.  
 (B) Since  $Q < K$ , the forward reaction is favored and the equilibrium shifts to the right.  
 (C) Since  $Q < K$ , the reverse reaction is favored and the equilibrium shifts to the left.  
 (D) Since  $Q > K$ , the reverse reaction is favored and the equilibrium shifts to the left.

# AP Multiple-Choice Review Questions

Questions 1–3 refer to the following:



- Which species are considered to be Brønsted-Lowry acids?
  - Only HF is a Brønsted-Lowry acid because it donates a proton.
  - HF and  $\text{H}_3\text{O}^+$  are both Brønsted-Lowry acids because they both donate protons.
  - HF and  $\text{F}^-$  are both Brønsted-Lowry acids because HF gains a proton while  $\text{F}^-$  donates a proton.
  - HF and  $\text{H}_2\text{O}$  are both Brønsted-Lowry acids because HF donates a proton while  $\text{H}_2\text{O}$  gains a proton.
- If the concentration of the HF in the reaction above is 0.1 M, what is an approximate pH of the solution?
  - 1
  - 2
  - 7
  - 9
- Which is the strongest base in this reaction?
  - $\text{F}^-$
  - $\text{H}_2\text{O}$
  - HF
  - $\text{H}_3\text{O}^+$
- Which of the following correctly ranks the species from weakest to strongest base?
 

HF ( $K_a = 7.1 \times 10^{-4}$ )  
 HCN ( $K_a = 6.2 \times 10^{-10}$ )  
 $\text{HClO}_2$  ( $K_a = 1.2 \times 10^{-2}$ )  
 $\text{NH}_4^+$  ( $K_a = 5.6 \times 10^{-10}$ )

  - $\text{CN}^- < \text{NH}_3 < \text{F}^- < \text{ClO}_2^- < \text{H}_2\text{O} < \text{NO}_3^-$
  - $\text{CN}^- < \text{NH}_3 < \text{F}^- < \text{ClO}_2^- < \text{NO}_3^- < \text{H}_2\text{O}$
  - $\text{H}_2\text{O} < \text{NO}_3^- < \text{ClO}_2^- < \text{F}^- < \text{NH}_3 < \text{CN}^-$
  - $\text{NO}_3^- < \text{H}_2\text{O} < \text{ClO}_2^- < \text{F}^- < \text{NH}_3 < \text{CN}^-$

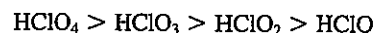
- At the normal body temperature of a human,  $37^\circ\text{C}$ , the equilibrium constant for the dissociation of water is higher than it is at  $25^\circ\text{C}$ , as shown in the equilibrium expression.

$$K_w = [\text{H}^+][\text{OH}^-] = 2.42 \times 10^{-14}$$

What is true of pure water at  $37^\circ\text{C}$ ?

- Water is neutral because the hydrogen and hydroxide ion concentrations are equal.
- Water is basic because the hydroxide ion concentration is greater than  $1 \times 10^{-7} \text{ M}$ .
- Water is acidic because the hydrogen ion concentration is greater than  $1 \times 10^{-7} \text{ M}$ .
- Water is neutral because the hydrogen and hydroxide ion concentrations are each  $1 \times 10^{-7} \text{ M}$ .

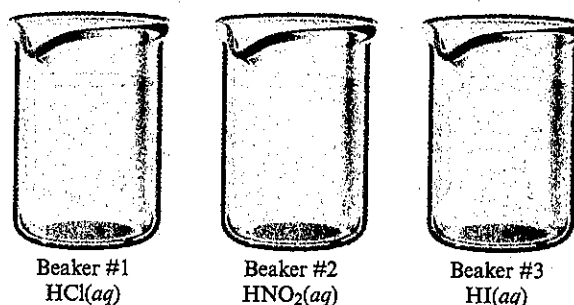
- The acid strength of the oxyacids of chlorine is as follows:



Which statement best explains this trend?

- The electrons in the H—O bond are pulled away from the hydrogen by the more electronegative oxygen, making the bond weaker. Additional oxygen atoms intensify this effect, making the H—O bond even weaker and increasing the degree of ionization.
- Oxygen is less electronegative than hydrogen. Additional oxygen atoms provide greater repulsion of the electrons and cause them to be even closer to the hydrogen atom, making the H—O bond weaker and increasing the degree of ionization.
- Extra electrons are always attracted to the central atom in a molecule. With more oxygen atoms, additional electrons are transferred to the chlorine atom. This weakens the H—O bond and increases the degree of ionization.
- Oxygen has six valence electrons. Each oxygen atom needs two additional electrons to fulfill its octet. These electrons are pulled from the H—O bond and cause the acid to ionize. More oxygen atoms require more electrons, so the degree of ionization increases.

Questions 7–9 refer to the following solutions:



Each beaker contains 100 mL of the indicated acidic solution, all with a pH of 3.00.

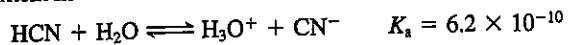
$$K_a \text{ for } \text{HNO}_2 = 4.0 \times 10^{-4}$$

- Which beaker would have the highest hydrogen ion concentration?
  - Beaker 1 has the highest hydrogen ion concentration.
  - Beaker 2 has the highest hydrogen ion concentration.
  - Beaker 1 and 3 are equally high.
  - All have the same hydrogen ion concentration.
- Which solution has the highest percent ionization?
  - Beaker 1 has the highest percent ionization.
  - Beaker 2 has the highest percent ionization.
  - Beakers 1 and 3 are equally high.
  - All have the same percent ionization.
- If 50 mL of 0.1 M NaOH was added to each beaker, which resulting solution would have the lowest pH?
  - Beaker 1 would have the lowest pH.
  - Beaker 2 would have the lowest pH.
  - Beakers 1 and 3 are equally low.
  - All would have the same pH.

10. A solution is prepared by mixing 500 mL of 1 M HCl with 500 mL of 0.01 M HNO<sub>3</sub>. What is the pH of the resulting solution?

(A) 0.0  
(B) between 0.0 and 1.0  
(C) 1.0  
(D) greater than 1.0

11. In a research project, a scientist adds 0.1 mole of HCN, 0.1 mole of H<sub>3</sub>O<sup>+</sup>, and 0.1 mole of CN<sup>-</sup> to water to make a total volume of 1 L. Will this reaction proceed to a greater extent in the forward direction or in the reverse direction?



(A) Forward; acids always dissociate in water.  
(B) Forward; the  $K$  value is less than 1.  
(C) Reverse; the  $K$  value is less than 1.  
(D) Reverse; water cannot be a reactant.

12. What is the conjugate acid of HPO<sub>4</sub><sup>2-</sup>?

(A) H<sub>3</sub>O<sup>+</sup>  
(B) PO<sub>4</sub><sup>3-</sup>  
(C) H<sub>2</sub>PO<sub>4</sub><sup>-</sup>  
(D) H<sub>3</sub>PO<sub>4</sub>

13. Bromothymol blue is a chemical indicator that turns blue at pH values greater than 7. In which of these solutions would a blue color be observed if 2 drops of bromothymol blue were added? The concentration of each solution is 0.10 M.  $K_a$  for HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>(aq) =  $1.8 \times 10^{-5}$ ;  $K_b$  for NH<sub>3</sub>(aq) =  $1.8 \times 10^{-5}$ .

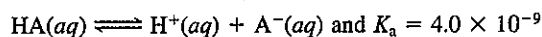
(A) NH<sub>4</sub>Cl  
(B) NaNO<sub>3</sub>  
(C) NH<sub>4</sub>C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>  
(D) NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>

14. A weak acid, HZ, has a  $K_a$  of  $1.0 \times 10^{-7}$ . What is the pH of a 0.10 M solution of HZ?

(A) 1.00  
(B) 3.50  
(C) 4.00  
(D) 7.00

## AP Multiple-Choice Review Questions

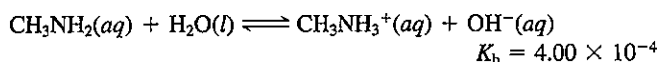
1. A 25.0-mL sample of an unknown monoprotic acid was titrated with 0.12 M NaOH. The student added 31.6 mL of NaOH and went past the equivalence point. Which procedure could be performed next to more accurately determine the concentration of the unknown acid?
  - (A) Back-titrate with additional NaOH to neutralize the additional HCl that was added.
  - (B) Back-titrate with additional HCl to neutralize the additional NaOH that was added.
  - (C) Start over again, being careful to stop the titration just before the equivalence point.
  - (D) Perform an additional two trials and average the volumes of the NaOH for all three trials.
2. A student uses acetic acid to titrate a solution of copper(I) hydroxide to determine the concentration of the copper(I) hydroxide. If 30.0 mL of 0.250 M acetic acid is needed to neutralize 15.0 mL copper(I) hydroxide, what is the molarity of the copper(I) hydroxide?
  - (A) 0.125 M
  - (B) 0.250 M
  - (C) 0.375 M
  - (D) 0.500 M
3. HA is a weak, monoprotic acid that dissociated according to the equation



If the initial concentration of HA is 0.10 M, find the concentration of  $\text{H}^+$ .

- (A)  $2.0 \times 10^{-4} M$
- (B)  $2.0 \times 10^{-5} M$
- (C)  $7.5 \times 10^{-8} M$
- (D)  $8.5 \times 10^{-10} M$

Questions 4 and 5 refer to the following reaction:



4. Determine the  $[\text{OH}^-]$  for 0.25 M methylamine,  $\text{CH}_3\text{NH}_2$ .
  - (A)  $2.0 \times 10^{-7} M$
  - (B)  $6.0 \times 10^{-5} M$
  - (C)  $1.0 \times 10^{-4} M$
  - (D)  $1.0 \times 10^{-2} M$
5. Determine the pH of the methylamine solution.
  - (A) 4.00
  - (B) 6.00
  - (C) 10.00
  - (D) 12.00

6. Solution A consists of 1.0 M  $\text{HC}_2\text{H}_3\text{O}_2$  ( $K_a = 1.8 \times 10^{-5}$ ), and Solution B consists of 1.0 M  $\text{HC}_2\text{H}_3\text{O}_2$  and 1.0 M  $\text{NaC}_2\text{H}_3\text{O}_2$ . Which of the following statements is true?
  - (A)  $\text{HC}_2\text{H}_3\text{O}_2$  undergoes a greater percent dissociation in Solution A than Solution B, and the pH of Solution A is lower than that of Solution B.
  - (B)  $\text{HC}_2\text{H}_3\text{O}_2$  undergoes a greater percent dissociation in Solution A than Solution B, and the pH of Solution A is higher than that of Solution B.
  - (C)  $\text{HC}_2\text{H}_3\text{O}_2$  undergoes a lower percent dissociation in Solution A than Solution B, and the pH of Solution A is lower than that of Solution B.
  - (D)  $\text{HC}_2\text{H}_3\text{O}_2$  undergoes a lower percent dissociation in Solution A than Solution B, and the pH of Solution A is higher than that of Solution B.
7. Consider 100.0 mL of 0.100 M aqueous solutions of each of the following acids: HCN ( $K_a = 6.2 \times 10^{-10}$ ), HF ( $K_a = 7.2 \times 10^{-4}$ ), HCl,  $\text{HC}_2\text{H}_3\text{O}_2$  ( $K_a = 1.8 \times 10^{-5}$ ). Each acid is titrated with 0.100 M NaOH(aq). Once the equivalence point is reached for each solution, rank the pH values from highest to lowest.
  - (A) HCl, HCN, HF,  $\text{HC}_2\text{H}_3\text{O}_2$
  - (B) HCN,  $\text{HC}_2\text{H}_3\text{O}_2$ , HF, HCl
  - (C) HCl, HF,  $\text{HC}_2\text{H}_3\text{O}_2$ , HCN
  - (D)  $\text{HC}_2\text{H}_3\text{O}_2$ , HCN, HCl, HF
8. You are asked to make 1.00 L of a solution buffered at a pH of 9.00. You are given 1.00 M HCN ( $K_a = 6.2 \times 10^{-10}$ ) and 1.00 M NaCN. Which of the following statements correctly describes the relative volumes of each solution to make such a buffer?
  - (A) The volumes of the 1.00 M HCN and the 1.00 M NaCN are equal.
  - (B) The volume of the 1.00 M HCN must be less than the volume of the 1.00 M NaCN.
  - (C) The volume of the 1.00 M HCN must be greater than the volume of the 1.00 M NaCN.
  - (D) There is no way to make a buffer solution at a pH of 9.00 with HCN and NaCN.
9. You are asked to make a buffered solution with a pH as close to 7.00 as possible by mixing equal volumes of 1.00 M solutions. Which of the following mixtures is the best choice?
  - (A) HF ( $K_a = 7.2 \times 10^{-4}$ ) and NaF
  - (B) HCN ( $K_a = 6.2 \times 10^{-10}$ ) and NaCN
  - (C) HOCl ( $K_a = 3.5 \times 10^{-8}$ ) and NaOCl
  - (D)  $\text{HC}_2\text{H}_3\text{O}_2$  ( $K_a = 1.8 \times 10^{-5}$ ) and  $\text{NaC}_2\text{H}_3\text{O}_2$
10. A certain buffer solution has a pH of 4.6. The weak acid used to make this solution, HA, has a  $\text{p}K_a$  of 3.2. Which statement best describes the relationship between the concentration of hydrogen ion,  $[\text{H}^+]$ , and the concentration of  $\text{A}^-$ ,  $[\text{A}^-]$ ?
  - (A)  $[\text{H}^+] > [\text{A}^-]$  because  $\text{pH} > \text{p}K_a$
  - (B)  $[\text{H}^+] > [\text{A}^-]$  because  $\text{pH} < \text{p}K_a$
  - (C)  $[\text{H}^+] < [\text{A}^-]$  because  $\text{pH} > \text{p}K_a$
  - (D)  $[\text{H}^+] < [\text{A}^-]$  because  $\text{pH} < \text{p}K_a$



11. Strong acids do not make good buffered solutions because
- (A) strong acids dissociate completely and the equilibrium lies far to the right.
  - (B) strong acids dissociate completely and the equilibrium lies far to the left.
  - (C) strong acids react completely with any base and the equilibrium lies far to the right.
  - (D) strong acids react completely with any base and the equilibrium lies far to the left.

Questions 12 and 13 refer to the following information:



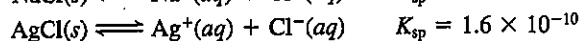
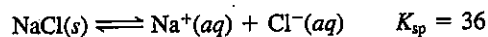
12. Which acid solution has a greater pH?
- (A) HA because it dissociates less than HX
  - (B) HA because it dissociates more than HX
  - (C) HX because it dissociates less than HA
  - (D) HX because it dissociates more than HA
13. How would diluting HA from 0.15 M to 0.005 M affect the pH of the solution?
- (A) The pH would decrease because the  $[H^+]$  decreases.
  - (B) The pH would decrease because the  $[H^+]$  increases.
  - (C) The pH would increase because the  $[H^+]$  decreases.
  - (D) The pH would increase because the  $[H^+]$  increases.
14. A 25.0-mL sample of 0.10 M  $HC_2H_3O_2$  is titrated with 0.10 M NaOH. What is the pH after 25.0 mL of NaOH have been added? The  $K_a$  value for  $HC_2H_3O_2$  is  $1.8 \times 10^{-5}$ .
- (A) 4.57
  - (B) 6.24
  - (C) 7.00
  - (D) 8.72
15. A 0.10 M HCl solution may be titrated with two different bases: 0.10 M NaOH or 0.10 M  $Ca(OH)_2$ . Which statement best describes the volumes of the bases necessary to reach the equivalence point?
- (A) Half as much NaOH is needed.
  - (B) Equal volumes of NaOH and  $Ca(OH)_2$  are needed.
  - (C) Twice as much  $Ca(OH)_2$  is needed.
  - (D) Twice as much NaOH is needed.

## AP Multiple-Choice Review Questions

1. A 0.010-mole sample of  $K_2SO_4$  is added to 1.0 L of each of two different solutions. One solution contains  $2.0 \times 10^{-3} M$   $Ba(NO_3)_2$ , and the other contains  $2.0 \times 10^{-3} M$   $AgNO_3$ . Which statement best describes what is observed?  $K_{sp}$  for  $BaSO_4 = 1.5 \times 10^{-9}$ ;  $K_{sp}$  for  $Ag_2SO_4 = 1.2 \times 10^{-5}$ .
  - (A)  $BaSO_4$  would precipitate, but  $Ag_2SO_4$  would not.
  - (B)  $Ag_2SO_4$  would precipitate, but  $BaSO_4$  would not.
  - (C) Both would precipitate.
  - (D) Neither would precipitate.
2. For which of the following can we directly compare their  $K_{sp}$  values to determine their relative solubilities?
  - (A)  $Ag_2CrO_4$  and  $AgBr$
  - (B)  $Ag_2SO_4$  and  $CaSO_4$
  - (C)  $PbCl_2$  and  $PbSO_4$
  - (D)  $ZnS$  and  $AgI$
3. The salt  $MX_2$  has a solubility of  $1.0 \times 10^{-4} M$ . Determine the  $K_{sp}$  for  $MX_2$ .
  - (A)  $1.0 \times 10^{-4}$
  - (B)  $1.0 \times 10^{-8}$
  - (C)  $1.0 \times 10^{-12}$
  - (D)  $4.0 \times 10^{-12}$
4. Three ionic salts,  $AX$ ,  $BX_2$ , and  $CX_3$ , each have a solubility of  $2 \times 10^{-5} M$ . Which of the following correctly ranks the  $K_{sp}$  of the three salts from least to greatest?
  - (A)  $CX_3 < BX_2 < AX$
  - (B)  $AX < BX_2 < CX_3$
  - (C)  $BX_2 < CX_3 < AX$
  - (D)  $AX < CX_3 < BX_2$
5. Aqueous solutions of  $NaCl$  and  $Na_2CrO_4$  are mixed and they do not react. To this mixture an aqueous solution of  $AgNO_3$  is added (dropwise). At first, a white solid forms. As the  $AgNO_3$  solution continues to be added, a yellow solid begins to form.  $AgCl(s)$  is white in color and  $Ag_2CrO_4(s)$  is yellow. Which of the following is the most accurate conclusion based on these results?
  - (A) The molar solubility of the  $NaCl$  is greater than the molar solubility of  $Na_2CrO_4$  because the white solid formed first.
  - (B) The molar solubility of the  $NaCl$  is less than the molar solubility of  $Na_2CrO_4$  because the white solid formed first.
  - (C) The molar solubility of  $AgCl$  is greater than the molar solubility of  $Ag_2CrO_4$  because the white solid formed first.
  - (D) The molar solubility of  $AgCl$  is less than the molar solubility of  $Ag_2CrO_4$  because the white solid formed first.
6. Barium iodate has a  $K_{sp}$  of  $4.0 \times 10^{-9}$ . What is the iodate ion concentration in a saturated solution of barium iodate?
  - (A)  $1.0 \times 10^{-3} M$
  - (B)  $2.0 \times 10^{-3} M$
  - (C)  $6.3 \times 10^{-5} M$
  - (D)  $2.0 \times 10^{-9} M$
7. Which of these salts would have increased solubility in a 0.10 M solution of  $HNO_3$ , compared with their solubilities in pure water at the same temperature?
  - (A)  $AgBr$
  - (B)  $Hg_2Cl_2$
  - (C)  $Mg(OH)_2$
  - (D)  $PbI_2$
8. When 0.10 mole of solid  $Ag_2C_2O_4$  is added to 1 L of pure water at  $25^\circ C$ , a saturated solution results. The solubility of  $Ag_2C_2O_4$  is  $2.1 \times 10^{-4} M$ . Which would be the correct setup to calculate the  $K_{sp}$  of  $Ag_2C_2O_4$ ?
  - (A)  $K_{sp} = (2.1 \times 10^{-4})(2.1 \times 10^{-4})$
  - (B)  $K_{sp} = (2.1 \times 10^{-4})^2(2.1 \times 10^{-4})$
  - (C)  $K_{sp} = \frac{(2.1 \times 10^{-4})(2.1 \times 10^{-4})}{0.10}$
  - (D)  $K_{sp} = \frac{(2.1 \times 10^{-4})^2(2.1 \times 10^{-4})}{0.10}$
9. Ten grams of  $Ca(OH)_2(s)$  is added, with stirring, to 100 mL of water, producing a saturated solution with solid  $Ca(OH)_2$  on the bottom of the beaker. Which is true?
  - (A) The addition of 30 drops of 3 M  $HCl$  will cause the  $K_{sp}$  of the reaction to decrease.
  - (B) The addition of 0.1 mole of solid  $Ca(NO_3)_2$  will cause some additional  $Ca(OH)_2$  to form.
  - (C) The addition of 0.1 mole of solid  $NaOH$  will cause some additional  $Ca(OH)_2$  to dissolve.
  - (D) The addition of 0.1 mole of solid  $Ca(OH)_2$  will cause the  $K_{sp}$  of the reaction to increase.
10. Solid sodium chloride was added to pure water slowly, with stirring, at  $25^\circ C$  until no more sodium chloride would dissolve. Solid remained on the bottom of the container, even after the solution was stirred repeatedly over 8 hours. After the solid was allowed to settle, some of the clear, colorless solution was carefully poured off into a flask. This flask was placed in a refrigerator at a temperature of  $4^\circ C$  for 2 hours. When the flask was removed from the refrigerator, a small amount of white solid was found to have appeared in the flask. What is the best explanation for this?
  - (A) Solids settle out of solutions over time.
  - (B)  $NaCl$  has an exothermic heat of solution.
  - (C) The  $K_{sp}$  of  $NaCl$  decreases with decreasing temperature.
  - (D) The  $K_{sp}$  of  $NaCl$  increases with decreasing temperature.
11. Which of the following statements is true concerning the relative solubility of silver chloride? All samples are at the same temperature.
  - (A)  $AgCl$  is less soluble in 1.0 M  $AgNO_3$  than it is in pure water.
  - (B)  $AgCl$  is less soluble in 1.0 M  $HNO_3$  than it is in pure water.
  - (C)  $AgCl$  is more soluble in 1.0 M  $AgNO_3$  than it is in pure water.
  - (D)  $AgCl$  is more soluble in 1.0 M  $HNO_3$  than it is in pure water.

12. The  $K_{sp}$  of a hypothetical metallic hydroxide, MOH, is  $1.0 \times 10^{-4}$ . What is the pH of a saturated solution of MOH?
- (A) 4.00  
(B) 8.00  
(C) 10.00  
(D) 12.00

13. The solubility equations and  $K_{sp}$  values for two different chloride salts are shown below.



What can be interpreted from this information?

- (A) The  $K_{sp}$  of AgCl is so small that AgCl is completely insoluble.  
(B) The  $K_{sp}$  of NaCl is so large that the reaction is not reversible.  
(C) With NaCl, the forward reaction is favored. The relatively large equilibrium constant tells us that the products are favored.  
(D) With AgCl, the forward reaction is favored. The relatively small equilibrium constant tells us that the products are favored.
14. The mineral fluorite is the main source of calcium fluoride.  $\text{CaF}_2$  has a solubility of  $2.2 \times 10^{-4} M$  in pure water. Which is a correct explanation for what occurs when solid  $\text{CaF}_2$  is dissolved in an acidic solution, rather than in pure water?
- (A) The solubility increases because HF is a weak acid.  
(B) The solubility increases because HF is a strong acid.  
(C) The solubility decreases because HF is a weak acid.  
(D) The solubility decreases because HF is a strong acid.

15. Aqueous solutions of  $\text{Na}_2\text{CO}_3$  and  $\text{Ca}(\text{NO}_3)_2$ , 0.10 M each, are combined. A white precipitate is observed in the container after mixing. The precipitate is filtered and carefully rinsed with distilled water to remove other ions. A sample of the precipitate is added to 100 mL of 0.1 M NaCl. A second sample of the precipitate is then added to 100 mL of 0.1 M HCl. What would be observed in each case?

	NaCl (0.1 M)	HCl (0.1 M)
(A)	Additional precipitate forms.	No visible reaction occurs.
(B)	No visible reaction occurs.	Gas is produced, and some precipitate dissolves.
(C)	No visible reaction occurs.	No visible reaction occurs.
(D)	Additional precipitate forms.	Gas is produced, and some precipitate dissolves.

## AP Multiple-Choice Review Questions

1. Consider the freezing of liquid water at  $-10^{\circ}\text{C}$  and 1 atm. For this process, what are the signs for  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$ ?

(A)	+	-	0
(B)	-	+	0
(C)	+	+	-
(D)	-	-	-

2. A 100-mL sample of water is placed in a coffee-cup calorimeter. Solid NaCl is then dissolved in the water. The temperature of the water decreases from  $20.5^{\circ}\text{C}$  to  $19.7^{\circ}\text{C}$  and is then allowed to return to room temperature ( $20.5^{\circ}\text{C}$ ). Determine the signs for  $\Delta H$  and  $\Delta S$  for the process of dissolving NaCl and  $\Delta G$  for the entire process at constant temperature.

(A)	+	-	0
(B)	-	+	0
(C)	+	+	-
(D)	-	-	-

3. Which reaction would have the most positive  $\Delta S^{\circ}$ ?

- (A)  $\text{CO(g)} + 2\text{H}_2\text{(g)} \rightarrow \text{CH}_3\text{OH(l)}$   
 (B)  $2\text{CH}_3\text{OH(g)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)} + 4\text{H}_2\text{O(g)}$   
 (C)  $\text{HCl(g)} + \text{NH}_3\text{(g)} \rightarrow \text{NH}_4\text{Cl(s)}$   
 (D)  $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O(s)} + 2\text{NH}_4\text{NO}_3\text{(s)} \rightarrow \text{Ba(NO}_3)_2\text{(s)} + 2\text{NH}_3\text{(g)} + 10\text{H}_2\text{O(l)}$

4. Solutions A and B are both clear and colorless. When Solution A is mixed with Solution B, the temperature of the mixture increases and a yellow precipitate is observed. What can be concluded from these observations?

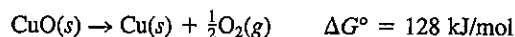
- (A) The reaction is thermodynamically favored (spontaneous) at all temperatures.  
 (B) The reaction is thermodynamically favored (spontaneous) only at high temperatures.  
 (C) The reaction is thermodynamically favored (spontaneous) only at low temperatures.  
 (D) The reaction is not thermodynamically favored (spontaneous) at any temperature.

Questions 5–8 refer to the following information:

The removal of copper from metallic ores has been a challenge since ancient times. Strong heating of copper(II) carbonate results in the formation of copper(II) oxide.

Although the decomposition of copper(II) oxide into copper metal and oxygen gas is not thermodynamically favorable under standard conditions, it may be made favorable by adding carbon to the mixture.

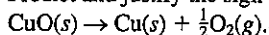
The resulting reaction is:  $2\text{CuO(s)} + \text{C(s)} \rightarrow 2\text{Cu(s)} + \text{CO}_2\text{(g)}$ .



5. Calculate  $\Delta G^{\circ}$  for the overall reaction.

- (A)  $-138 \text{ kJ/mol}$   
 (B)  $-266 \text{ kJ/mol}$   
 (C)  $522 \text{ kJ/mol}$   
 (D)  $650 \text{ kJ/mol}$

6. Predict and justify the sign of  $\Delta S^{\circ}$  for the reaction



- (A)  $\Delta S$  is positive because  $\Delta G$  is positive.  
 (B)  $\Delta S$  is negative because  $\Delta G$  is positive.  
 (C)  $\Delta S$  is positive because the products have more moles of gas than the reactant.  
 (D)  $\Delta S$  is negative because the products have more moles of gas than the reactant.

7. Why is the overall process thermodynamically favorable?

- (A) Carbon serves as a catalyst to lower the activation energy of the reaction.  
 (B) The process involves coupling a very thermodynamically favorable reaction with one that is not thermodynamically favored.  
 (C) When two reactions are coupled, free energy is always released.  
 (D) The addition of carbon speeds up the reaction because powdered carbon has a large surface area.

8. Which statement is correct about the value of  $K$  for the reaction  $2\text{CuO(s)} + \text{C(s)} \rightarrow 2\text{Cu(s)} + \text{CO}_2\text{(g)}$  at standard conditions?

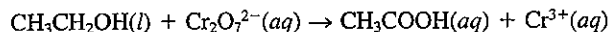
- (A)  $K$  will be less than 1.  
 (B)  $K$  will be 0.  
 (C)  $K$  will be between 0 and 1.  
 (D)  $K$  will be greater than 1.

9. Under normal conditions, an iron nail rusts so slowly that the reaction is not easily observed. What must be true?
- (A) The reaction occurs, but very slowly.
  - (B) The product of the reaction is an invisible gas.
  - (C) The reaction does not occur without a catalyst.
  - (D) The reaction is not thermodynamically favorable.
10. Calculate the  $\Delta G^\circ$  for the following equation:
- $$2\text{SO}_2(g) + \text{O}_2(g) \rightarrow 2\text{SO}_3(g)$$
- $\Delta G_f^\circ$  for  $\text{SO}_2 = -300 \text{ kJ/mol}$   
 $\Delta G_f^\circ$  for  $\text{SO}_3 = -371 \text{ kJ/mol}$
- (A)  $-71 \text{ kJ/mol}$
  - (B)  $-142 \text{ kJ/mol}$
  - (C)  $71 \text{ kJ/mol}$
  - (D)  $671 \text{ kJ/mol}$

## AP Multiple-Choice Review Questions

Questions 1–3 refer to the following:

Alcohols are organic compounds containing a hydroxyl ( $\text{—OH}$ ) group. When a solution containing dichromate ions is added to most alcohols, chromium(III) ions are formed. The color of the solution changes from bright orange to green.



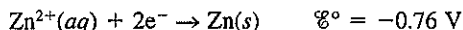
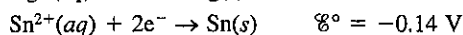
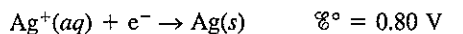
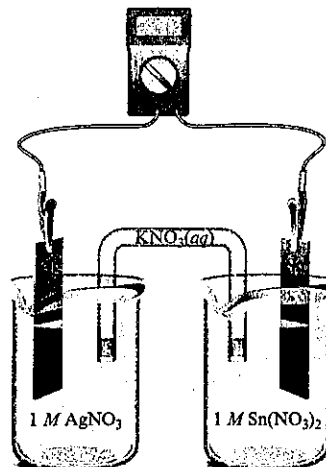
The *unbalanced* reaction above shows ethanol reacting with the dichromate ion to produce acetic acid and the chromium(III) ion. This reaction occurs in acidic solution and is the chemical reaction used in a Breathalyzer that determines a person's blood alcohol level from the ethanol vapor present in his or her breath.

A kinetic study was conducted to determine the order of the  $\text{Cr}_2\text{O}_7^{2-}$  ion in the rate law. A large excess of alcohol and hydrogen ions was used to ensure that their concentrations did not limit the reaction. The concentration of dichromate was followed spectrophotometrically, and the absorbance and time values were recorded.

- What is the coefficient for water in the balanced redox reaction?  
(A) 6  
(B) 11  
(C) 14  
(D) 19
- Which element is oxidized in the reaction?  
(A) C  
(B) Cr  
(C) H  
(D) O
- In the kinetic study, the natural logarithms of the absorbance values were plotted versus time, resulting in a straight line. What does this indicate about the order of the reaction with respect to the dichromate ion?  
(A) The reaction is zero order in dichromate.  
(B) The reaction is first order in dichromate.  
(C) The reaction is second order in dichromate.  
(D) The order cannot be determined from this graph.
- How many moles of solid chromium can be deposited from a  $\text{CrCl}_3$  solution when a steel wrench is electroplated with a current of 3.0 amps for 965 seconds?



Questions 5–9 refer to the following electrochemical cell and reduction potentials:

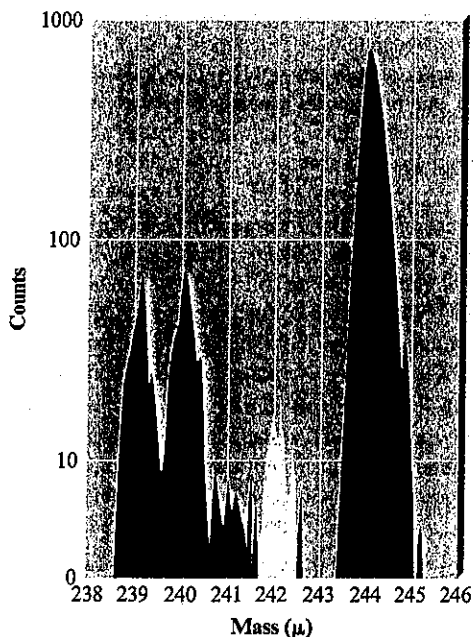


- Determine the  $\mathcal{E}_{\text{cell}}^\circ$  for the voltaic cell pictured above.  
(A) 0.66V  
(B) 0.94V  
(C) -0.94V  
(D) 1.74V
- Which of these changes would increase the value of  $\mathcal{E}_{\text{cell}}$ ?  
(A) Add 50.0 mL of water to each beaker.  
(B) Add 0.10 mole of  $\text{NaCl}(s)$  to the left beaker, producing a precipitate.  
(C) Increase the temperature of each solution by  $20^\circ\text{C}$ .  
(D) Add 1.5 g of  $\text{AgNO}_3(s)$  to the left beaker.
- Which of the following is true regarding the salt bridge in this voltaic cell?  
(A) Electrons travel through the salt bridge from the cathode to the anode.  
(B) Electrons travel through the salt bridge from the anode to the cathode.  
(C) Potassium ions travel to the anode, and nitrate ions travel to the cathode.  
(D) Potassium ions travel to the cathode, and nitrate ions travel to the anode.
- If the reverse reaction was desired, how could it be obtained in the laboratory?  
(A) Increase the temperature and increase the concentration of the  $\text{Sn}^{2+}$ .  
(B) Apply an electrical potential less than the  $\mathcal{E}_{\text{cell}}^\circ$  for the forward reaction.  
(C) Apply an electrical potential greater than the  $\mathcal{E}_{\text{cell}}^\circ$  for the forward reaction.  
(D) The reverse reaction is not thermodynamically favored and cannot occur.

9. If the tin electrode was replaced with a strip of zinc, how would the cell voltage change?
- (A) increase
  - (B) decrease
  - (C) no change
  - (D) become zero
10. When electricity is passed through molten sodium chloride, solid sodium metal is formed at the cathode and chlorine gas is formed at the anode. Which of the following is true regarding this reaction?
- (A)  $\Delta G$  is positive.
  - (B) The reaction is at equilibrium.
  - (C) Electrons travel from the cathode to the anode.
  - (D) The equilibrium constant has a value greater than 1.

## AP Multiple-Choice Review Questions

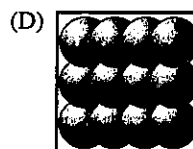
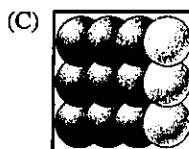
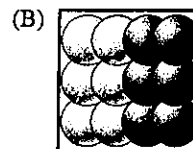
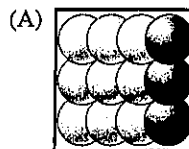
- $^{87}\text{Sr}$  is a radiotracer used in studying bones. It decays by a first-order process and has a half-life of almost 3 hours. Approximately what percentage of radioactive material remains after a day?
  - 0.3%
  - 1%
  - 3%
  - 10%
- The observed first-order rate of decay of carbon-14 in living material is 13.6 counts per minute per gram of carbon. An old wooden cup was discovered and found to give 10.9 counts per minute per gram of carbon. Approximately how old is the cup? For  $^{14}\text{C}$ ,  $t_{1/2} = 5730$  years.
  - 1800 years
  - 4900 years
  - 5700 years
  - 11,000 years
- The mass spectrum of a sample of radioactive plutonium recovered from a nuclear reactor is shown below.



Using the graph, determine the number of neutrons in the isotope of plutonium having the greatest abundance in this sample.

- 94
- 150
- 242
- 244

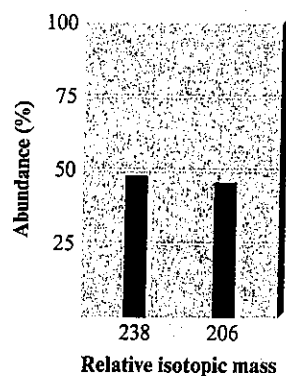
- Plutonium-243 decays into americium-243 by first-order kinetics. The half-life of  $^{243}\text{Pu}$  is 5 hours. If the white spheres represent atoms of  $^{243}\text{Pu}$  and the gray spheres represent  $^{243}\text{Am}$ , which diagram would show the ratio of atoms of  $^{243}\text{Pu}$  to  $^{243}\text{Am}$  after 10 hours?



- Bismuth-214 is a radioactive isotope that may decay into polonium-214 or into thallium-210. Which isotope would have the most similar *chemical* reactivity to bismuth-214?
  - lead-214
  - polonium-214
  - thallium-210
  - bismuth-210
- Gold-198 is a radioactive isotope that is used to treat several types of cancer. Its first-order decay has a half-life of 2.7 days. How many grams must a physician order for a treatment that will begin in 11 days, if approximately 15 grams of gold-198 is needed for the treatment?
  - 15 g
  - 30 g
  - 60 g
  - 240 g
- The half-life for the first-order nuclear decay of a 10.0-g sample of strontium-90 is 28 years. What is the half-life of a 5.0-g sample of strontium-90?
  - 7 years
  - 14 years
  - 28 years
  - 56 years
- Cesium-137 is a common radioactive product of fission that has many uses in industry and medicine. The half-life of this decay is 30. years. Determine the specific rate constant for this first-order decay.
  - $0.023 \text{ yr}^{-1}$
  - $30. \text{ yr}^{-1}$
  - $43 \text{ yr}^{-1}$
  - $140 \text{ yr}^{-1}$



9. Minerals containing uranium can be dated to determine their approximate age by analyzing the isotopes of lead found in the sample. Uranium-236 decays to lead-206. Lead-206 is not a common isotope of lead, so any lead-206 found in a mineral must come from the decay of uranium-236. A mineral was analyzed, and its mass spectrum is shown below.



If the radioactive decay of uranium-236 is first order with a half-life of 4.5 billion years, estimate the age of the sample.

- (A) 2.3 billion years
- (B) 4.5 billion years
- (C) 6.8 billion years
- (D) 9.0 billion years

10. Radioactive decay displays first-order kinetics. If the decay of iodine-131 is measured over time, which of these graphs will show a straight line?

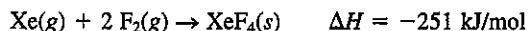
- (A) mass of  $^{131}\text{I}$  versus time
- (B) natural logarithm of mass of  $^{131}\text{I}$  versus time
- (C) reciprocal of mass of  $^{131}\text{I}$  versus time
- (D) mass of  $^{131}\text{I}$  versus reciprocal time

## AP Multiple-Choice Review Questions

Questions 1–4 refer to the following information:

The noble gas xenon was not discovered until 1898. It is obtained in very small quantities by distillation of the oxygen in air. Initially thought to be completely inert, the first xenon compound was made in 1962. Many different compounds have since been made from xenon, as well as from argon, krypton, and radon.

Xenon tetrafluoride was one of the first compounds synthesized from xenon by the following reaction:



Xenon tetrafluoride reacts readily with water according to the following reaction:



- What is the molecular geometry of xenon tetrafluoride?
  - tetrahedral
  - octahedral
  - square pyramidal
  - square planar
- What conditions would maximize the yield in the reaction for the formation of xenon tetrafluoride?
  - high temperature, high pressure
  - high temperature, low pressure
  - low temperature, high pressure
  - low temperature, low pressure
- If 103.5 g of  $\text{XeF}_4$  is reacted with excess water, how many moles of hydrofluoric acid are produced? Molar mass of  $\text{XeF}_4 = 207 \text{ g/mol}$ .
  - 0.125 mol
  - 0.500 mol
  - 1.00 mol
  - 2.00 mol
- The boiling points of the noble gases are shown in the table below. What is the best explanation as to why the boiling point of xenon is the highest in its group?

	Helium	Neon	Argon	Krypton	Xenon
Boiling Point	-269°C	-246°C	-186°C	-153°C	-107°C

- Xe atoms are polar, whereas other noble gases are nonpolar.
- Xe has the highest atomic mass in the group; thus it has a lower velocity.
- Xe has more electrons than the others, making it more polarizable.
- Xe is at the bottom of its group; boiling point always increases going down a group.

- Milk of Magnesia contains magnesium hydroxide and is often used as an antacid. Estimate the pH of a  $1.0 \times 10^{-3} \text{ M}$  solution of  $\text{Mg(OH)}_2$ .
  - 2.70
  - 3.00
  - 11.00
  - 11.30
- The  $K_{sp}$  of magnesium hydroxide is  $8.9 \times 10^{-12}$ . If 0.010 mole of  $\text{Mg(OH)}_2$  is added to 1.00 L of water, will it all dissolve?
  - Yes, it will all dissolve because  $Q$  is less than  $K$ .
  - Yes, it will all dissolve because  $Q$  is greater than  $K$ .
  - No, it will not all dissolve because  $Q$  is less than  $K$ .
  - No, it will not all dissolve because  $Q$  is greater than  $K$ .
- The reduction potentials of three alkali metals are given in the table below, along with the reduction potential of water. Given that reactions with more positive cell potentials are more thermodynamically favorable, what is the best explanation for the fact that the reaction of lithium with water occurs more slowly than the reaction of either sodium or potassium with water?

Alkali Metal	Reduction Half-Reaction	Reduction Potential (V)
Li	$\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$	-3.05 V
Na	$\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$	-2.71 V
K	$\text{K} \rightarrow \text{K}^+ + \text{e}^-$	-2.92 V
	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	-0.83 V

- Even though the reaction of lithium with water is thermodynamically favorable, it is kinetically slow.
  - The reaction of lithium with water requires a catalyst, whereas the reactions of potassium and sodium do not.
  - Reactivity increases going down a group of the periodic table. Lithium is above sodium and potassium in Group I.
  - The reactions of sodium and potassium with water produce hydrogen gas, whereas the reaction of lithium with water does not.
- Which of these compounds is most likely to consist of ionic bonds?
    - $\text{ClF}_3$
    - $\text{Rb}_2\text{O}$
    - $\text{PH}_3$
    - $\text{SnCl}_4$
  - Sodium reacts in a 1:1 ratio with bromine to form  $\text{NaBr}$ , whereas magnesium reacts in a 1:2 ratio with fluorine to form  $\text{MgF}_2$  and aluminum reacts in a 1:3 ratio with chlorine to form  $\text{AlCl}_3$ . What compound is formed when barium reacts with iodine?
    - $\text{BaI}$
    - $\text{BaI}_2$
    - $\text{BaI}_3$
    - $\text{BaI}_4$

10. The alkali metals are not found free in nature, only chemically combined with other elements in compounds. Why is this true?
- (A) Alkali metals have a full valence shell of electrons and are quite stable.
  - (B) Alkali metals are extremely reactive because of their low ionization energies.
  - (C) Alkali metals all have a large size in comparison to other elements in their period.
  - (D) Alkali metals have very positive reduction potentials and are thus easily reduced.
11. Atomic size generally \_\_\_\_\_ across a row and generally \_\_\_\_\_ down a column for representative elements on the periodic table.
- (A) increases; increases
  - (B) increases; decreases
  - (C) decreases; increases
  - (D) decreases; decreases
12. How many of the following are covalent hydrides?
- NH<sub>3</sub>   CH<sub>4</sub>   H<sub>2</sub>O   LiH
- (A) 1
  - (B) 2
  - (C) 3
  - (D) 4
13. Which of the following alkaline earth metals has the highest ionization energy?
- (A) beryllium
  - (B) barium
  - (C) magnesium
  - (D) strontium
14. Which group on the periodic table forms hydrides of the general formula H<sub>2</sub>X?
- (A) Group 6A
  - (B) Group 5A
  - (C) Group 4A
  - (D) Group 2A

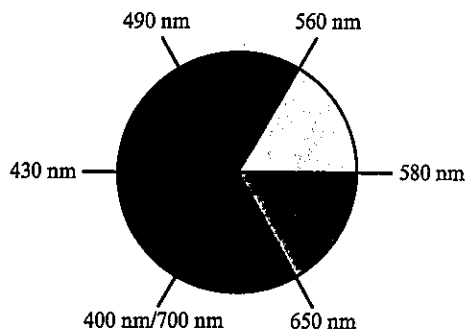
## AP Multiple-Choice Review Questions

Questions 1–5 refer to the following information:

Manganese is added to all steel in small quantities to increase the strength and hardness of the steel. The amount of manganese in a steel sample can be analyzed by a process where the steel is dissolved in nitric acid. The manganese present is then oxidized by potassium periodate to convert all of the manganese into the purple-colored permanganate ion.

The reaction is as follows:  $2\text{Mn}^{2+}(aq) + 5\text{IO}_4^-(aq) + 3\text{H}_2\text{O}(l) \rightleftharpoons 2\text{MnO}_4^-(aq) + 5\text{IO}_3^-(aq) + 6\text{H}^+(aq)$

- When solid manganese is dissolved in nitric acid, the  $\text{Mn}^{2+}$  ion is formed. Choose the correct electron configuration for the  $\text{Mn}^{2+}$  ion.
  - $[\text{Ar}]3d^5$
  - $[\text{Ar}]4s^23d^3$
  - $[\text{Ar}]4s^23d^5$
  - $[\text{Ar}]4s^23d^7$
- Which element is reduced in the reaction shown above?
  - hydrogen
  - iodine
  - manganese
  - oxygen
- If 20.00 mL of 0.100 M potassium periodate were needed to react completely with a sample containing  $\text{Mn}^{2+}$ , how many moles of  $\text{MnO}_4^-$  would be produced?
  - $1.00 \times 10^{-4}$  mole
  - $2.00 \times 10^{-4}$  mole
  - $5.00 \times 10^{-4}$  mole
  - $8.00 \times 10^{-4}$  mole
- The solution containing the permanganate ion can be analyzed spectrophotometrically to determine the concentration of permanganate. The colorimeter to be used has only four available wavelengths. Which wavelength should be chosen to get the maximum absorbance of light in the permanganate sample?



- 430 nm
- 470 nm
- 565 nm
- 635 nm

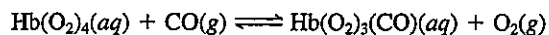
- Steel is an alloy of iron and other elements. It always contains carbon and manganese and can contain other elements depending on the desired qualities of the steel.

Which correctly lists the type of alloy formed by the carbon and the manganese with the iron in the steel?

(A)	Substitutional	Substitutional
(B)	Substitutional	Interstitial
(C)	Interstitial	Substitutional
(D)	Interstitial	Interstitial

- A visible light spectrophotometer would best be used in which of these situations?
  - to determine the isotopic composition of a sample of carbon
  - to determine the concentration of a solution of copper(II) nitrate
  - to determine the electron configuration of a sample of nickel
  - to determine the bonding present in an organic compound
- Which of these sets of elements show the most similar first ionization energies?
  - C, N, O, F
  - F, Cl, Br, I
  - Fe, Co, Ni, Cu
  - He, Ne, Ar, Kr
- The atomic radii of the transition metals do not vary much across a period. How can this best be explained?
  - Electrons in a transition metal all experience the same nuclear charge.
  - Electrons are being added to new energy levels, further from the nucleus.
  - Electrons are added to the same energy level as the number of protons increases.
  - Electrons are being added to inner *d* orbitals rather than to outer energy levels.
- Solid platinum is often used to increase the rate of a chemical reaction. How would Pt(s) most likely accomplish this?
  - The solid acts as an enzyme to catalyze biological reactions.
  - The metal directly participates in the reaction mechanism but is not a reactant or product.
  - It acts as a site for the reactants to temporarily bind to during the reaction process.
  - It provides extra energy for the reaction, resulting in more particles having the activation energy.

10. The oxygen in blood is carried by a large iron-containing protein called hemoglobin (Hb). Carbon monoxide also reacts with hemoglobin. The equilibrium constant for the reaction of carbon monoxide with hemoglobin is approximately 200 times larger than that for the reaction of oxygen with hemoglobin. From one to all four of the oxygen molecules can be replaced with a carbon monoxide molecule. The following reaction shows only one oxygen molecule replaced with carbon monoxide.



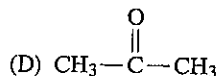
Using this information, which of the following treatments might be highly effective for carbon monoxide poisoning, if started immediately?

- (A) Have the patient breathe pure oxygen.
- (B) Add additional iron to the patient's diet.
- (C) Remove 250 mL of blood from the patient.
- (D) Decrease the pressure of the air that the patient is breathing.

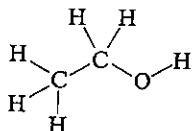
## AP Multiple-Choice Review Questions

1. An aqueous solution of which of these compounds would have a pH of greater than 8.0?

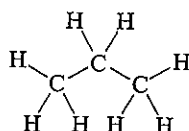
(A)  $\text{CH}_3\text{NH}_2$   
 (B)  $\text{CH}_3\text{COOH}$   
 (C)  $\text{CH}_3\text{CH}_2\text{OH}$



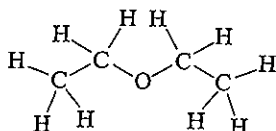
2. The boiling points of four different organic compounds whose structures are shown were determined and are given in the table below. Which boiling point is most likely that of ethanol?



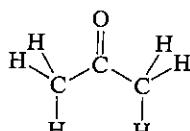
ethanol



propane



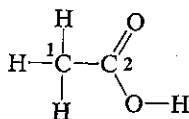
diethyl ether



acetone

compound	boiling point
(A)	$-42^\circ\text{C}$
(B)	$35^\circ\text{C}$
(C)	$56^\circ\text{C}$
(D)	$78^\circ\text{C}$

Questions 3 and 4 refer to the following acetic acid molecule:



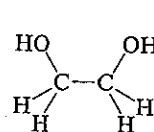
3. Predict the approximate bond angle around the carbon labeled 1 in the acetic acid molecule.

(A)  $90^\circ$   
 (B)  $109.5^\circ$   
 (C)  $120^\circ$   
 (D)  $180^\circ$

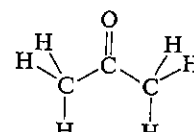
4. What is the expected hybridization of the carbon labeled 2 in the acetic acid molecule?

(A)  $sp$   
 (B)  $s^2p$   
 (C)  $sp^2$   
 (D)  $sp^3$

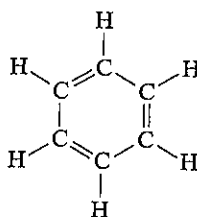
5.



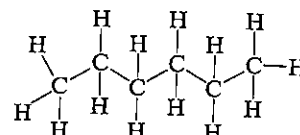
#1



#2



#3

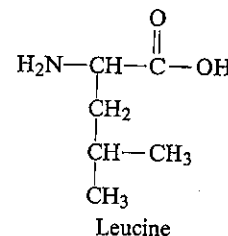
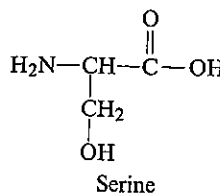
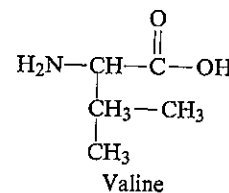
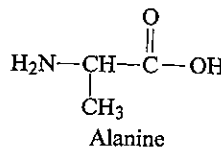


hexane

The first three organic compounds shown above were tested for their solubility both in water and also in hexane. The results are shown in the table below. Which of these conclusions could be predicted from these data?

compound	Observations of Solubility in Water	Observations of Solubility in Hexane
#1	Very soluble	Insoluble
#2	Soluble	Soluble
#3	Insoluble, forms separate layer	Very soluble

- (A) Compound 1 = benzene, compound 2 = acetone, compound 3 = ethylene glycol  
 (B) Compound 1 = ethylene glycol, compound 2 = acetone, compound 3 = benzene  
 (C) Compound 1 = acetone, compound 2 = benzene, compound 3 = ethylene glycol  
 (D) Compound 1 = benzene, compound 2 = ethylene glycol, compound 3 = acetone
6. Which of these amino acids would you expect to exhibit the most hydrophilic behavior?

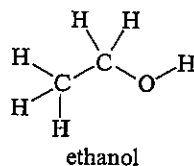


- (A) alanine  
 (B) valine  
 (C) serine  
 (D) leucine

7. Which of these compounds would you predict to have the highest boiling point?

(A)  $\text{CO}_2$   
(B)  $\text{CH}_4$   
(C)  $\text{CCl}_4$   
(D)  $\text{CBr}_4$

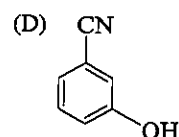
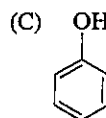
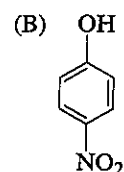
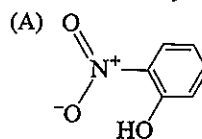
8.



A 25-mL sample of ethanol is slowly heated to  $80^\circ\text{C}$  using a hot plate. The volume of ethanol in the beaker gradually decreases to 10 mL. What is the best conclusion for what is occurring to the ethanol?

- (A) A chemical change is occurring because the covalent bonds are being broken.  
(B) A chemical change is occurring because the hydrogen bonds are being broken.  
(C) A physical change is occurring because the covalent bonds are being broken.  
(D) A physical change is occurring because the hydrogen bonds are being broken.

9. The four compounds shown all exhibit *intermolecular* hydrogen bonding. Which one of these compounds can also form *intramolecular* hydrogen bonds?



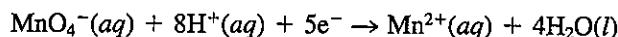
10. There are two possible types of secondary structures in proteins: an  $\alpha$ -helix and a pleated sheet. In the case of an  $\alpha$ -helix, the polypeptide twists into a helix. What enables the formation and stability of the  $\alpha$ -helix secondary structures?

- (A) Hydrogen bonds form between adjacent proteins.  
(B) Covalent bonds form between adjacent proteins.  
(C) Hydrogen bonds form between amino acids in the same protein.  
(D) Covalent bonds form between amino acids in the same protein.

## A7.1 | Simple Oxidation–Reduction Titrations

In Section 4.8 we discussed volumetric analysis, specifically acid–base titrations. Oxidation–reduction reactions (discussed in Section 4.9) can also be used for volumetric analytical procedures. For example, a reducing substance can be titrated with a solution of a strong oxidizing agent or vice versa. Three of the most frequently used oxidizing agents are aqueous solution of *potassium permanganate* ( $\text{KMnO}_4$ ), *potassium dichromate* ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), and *cerium hydrogen sulfate* [ $\text{Ce}(\text{HSO}_4)_4$ ].

The strong oxidizing agent, the permanganate ion ( $\text{MnO}_4^-$ ), can undergo several different reactions. The reaction that occurs in acidic solution is the one most commonly used:



Permanganate has the advantage of being its own indicator—the  $\text{MnO}_4^-$  ion is intensely purple, and the  $\text{Mn}^{2+}$  ion is almost colorless. As long as some reducing agent remains in the solution being titrated, the solution remains colorless (assuming all other species present are colorless), because the purple  $\text{MnO}_4^-$  ion being added is converted to the essentially colorless  $\text{Mn}^{2+}$  ion. However, when all the reducing agent has been consumed, the next drop of permanganate titrant will turn the solution being titrated light purple (pink). Thus, the endpoint (where the color change indicates the titration should stop) occurs approximately one drop beyond the stoichiometric point (the actual point at which all the reducing agent has been consumed).

The example problem below describes a typical volumetric analysis using permanganate.

### Example

Iron ores often involve a mixture of oxides and contain both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions. Such an ore can be analyzed for its iron content by dissolving it in acidic solution, reducing all the iron to  $\text{Fe}^{2+}$  ions, and then titrating with a standard solution of potassium permanganate. In the resulting solution,  $\text{MnO}_4^-$  is reduced to  $\text{Mn}^{2+}$ , and  $\text{Fe}^{2+}$  is oxidized to  $\text{Fe}^{3+}$ . A sample of iron ore weighing 0.3500 g was dissolved in acidic solution, and all the iron was reduced to  $\text{Fe}^{2+}$ . Then the solution was titrated with a  $1.621 \times 10^{-2} M$   $\text{KMnO}_4$  solution. The titration required 41.56 mL of the permanganate solution to reach the light purple (pink) endpoint. Determine the mass percent of iron in the iron ore.

### Solution

› What are we trying to solve?

We are asked to determine the mass percent of iron in an iron ore.

› What does this mean?

$$\text{Mass percent of iron} = \frac{\text{mass of iron}}{\text{mass of iron ore}} \times 100\%$$

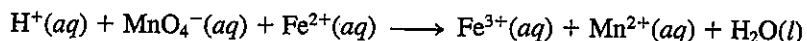
We know that the mass of the mixture is 0.3500 g, so we change the question to “*What is the mass of the iron?*”

All of the iron metal is converted to  $\text{Fe}^{2+}$ , which is reacted with a known volume and molarity of  $\text{MnO}_4^-$ . From volume and molarity we can get moles, and by using the mole ratio in a balanced equation, we can determine the moles of iron. We convert from moles to mass using the atomic mass of iron.

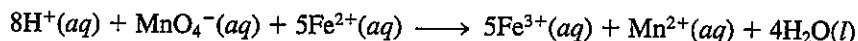
From the problem it is obvious that this is a redox reaction, so we will need to balance the equation accordingly.



First, we write the unbalanced equation for the reaction:



Using the half-reaction method, we balance the equation:



The number of moles of  $\text{MnO}_4^-$  ion required in the titration is found from the volume and concentration of permanganate solution used:

$$41.56 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1.621 \times 10^{-2} \text{ mol MnO}_4^-}{\text{L}} = 6.737 \times 10^{-4} \text{ mol MnO}_4^-$$

The balanced equation shows that five times as much  $\text{Fe}^{2+}$  as  $\text{MnO}_4^-$  is required:

$$6.737 \times 10^{-4} \text{ mol MnO}_4^- \times \frac{5 \text{ mol Fe}^{2+}}{1 \text{ mol MnO}_4^-} = 3.368 \times 10^{-3} \text{ mol Fe}^{2+}$$

Thus the 0.3500-g sample of iron ore contained  $3.368 \times 10^{-3}$  mole of iron. The mass of iron present is

$$3.368 \times 10^{-3} \text{ mol Fe} \times \frac{55.85 \text{ g Fe}}{1 \text{ mol Fe}} = 0.1881 \text{ g Fe}$$

The mass percent of iron in the iron ore is

$$\frac{0.1881 \text{ g}}{0.3500 \text{ g}} \times 100\% = 53.74\%$$

## A7.2 | Thermal Equilibrium, the Kinetic Molecular Theory, and the Process of Heat

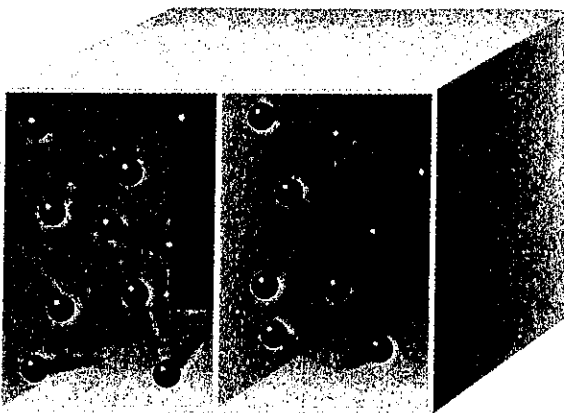
In Chapter 6 we defined heat as a transfer of energy between two objects due to a temperature difference. Experience shows that when two objects at different temperatures are in contact, they will eventually reach the same intermediate temperature. For example, suppose you and a friend are each enjoying a beverage. You are drinking a cold glass of lemonade while your friend has a hot cup of tea. If you allow the drinks to sit for a long enough period of time, the temperature of the tea will decrease and the temperature of the lemonade will increase. Eventually the temperatures of tea and the lemonade will be the same as room temperature. Energy is transferred in the form of heat from the hot tea to the surroundings (air in the room) and from the surroundings to the cold lemonade. Thus, we see that energy is always transferred from the “hot body” to the “cold body.” How does this process occur?

To answer this, let's consider a relatively simple system—two samples of gases, each at a different temperature and in contact as shown below. The wall separating the two samples is a thin membrane.

Recall from Chapter 5 that temperature is a measure of the kinetic energy of a sample of gas. That is, temperature is an index of the random motions of the particles of the gas. A higher temperature means that the gas has a greater average kinetic energy, which gives rise to a higher average velocity of the gas particles.

The gas particles in the left side of the container are at a higher temperature and thus moving at a greater average velocity than the particles in the right side (velocity is represented by the “tails” on the particles in Fig. A.8). Consider what happens when a particle in the left side (“hot”) collides with the membrane at the same time and on the exact opposite side as a particle on the right side (“cold”). Energy will be trans-

Figure A.8



ferred from the faster-moving particle on the left side to the slower-moving particle on the right side. The particle with the higher initial velocity will slow down, while the particle with the lower initial velocity will speed up. As this process continues, the average kinetic energy on the left side will decrease and the average kinetic energy on the right side will increase. Eventually, the average kinetic energy on each side will be equal, and the temperature of the gas samples will be the same. When this happens, the particles will still be in motion, but they will be moving with the same average velocity.

Although this is perhaps easier to visualize with gas particles striking a shared wall, a similar process occurs with solids and liquids. Atoms and molecules are always in constant motion (even if that motion is merely vibrating such as in a solid lattice). Temperature is a measure of the average kinetic energy of particles in solids and liquids as well as in gases. For any “hot body” in thermal contact with a “cold body,” energy is transferred as the initially faster particles decrease in motion and the initially slower molecules increase in motion. Therefore, the samples will eventually reach thermal equilibrium. That is, the particles will have the same average kinetic energy and thus the same temperature.

### A7.3 | Intermolecular Forces: The Difference Between Real and Ideal Gases

In Chapter 5 we discussed that no real gas exactly follows the ideal gas law, although many gases come very close at low pressure and/or high temperature. The van der Waals equation was developed to correct for the assumptions made in the kinetic molecular theory.

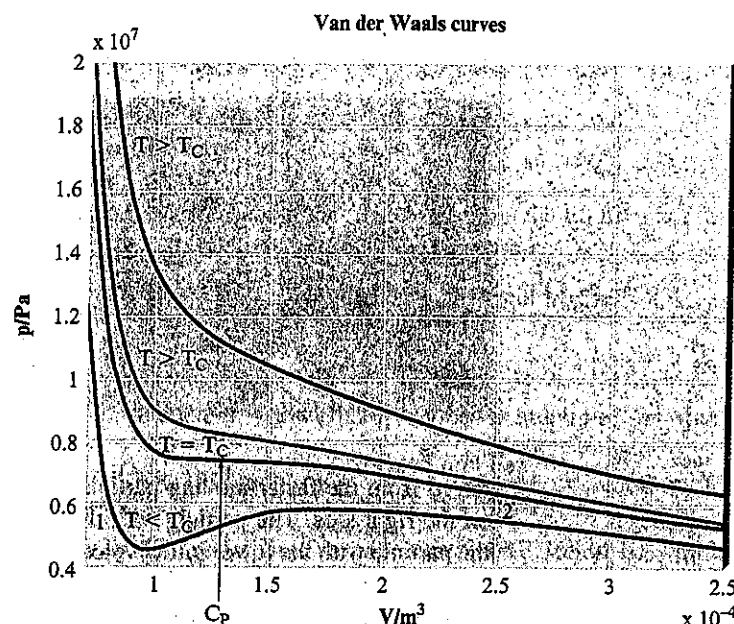
One assumption is that the particles of a gas are assumed to exert no forces on each other. From Chapter 10, we know that all gas particles exhibit attractive forces, termed *intermolecular forces*, and that the strength of these varies depending on the nature of the particles.

For example, consider  $\text{He}(g)$  and  $\text{H}_2\text{O}(g)$ . The helium atoms exhibit the relatively weak London dispersion forces, whereas water molecules exhibit the much stronger hydrogen bonding. We would expect, then, that helium gas would behave much more ideally than water vapor. This is supported by van der Waals constants. Recall that to account for the interparticle attractions of a gas, van der Waals added a correction factor to the observed pressure as follows:

$$P_{\text{ideal}} = P_{\text{obs}} + a\left(\frac{n}{V}\right)^2$$

Because gas particles attract one another, the particles will collide with the walls of the container slightly less often than they would ideally, so we need to add a correc-

Figure A.9



tion factor to make up for this. Although the constant  $a$  in the correction factor was empirically determined by van der Waals, it turns out that the values of this constant generally serve as indexes of the strength of the intermolecular forces exhibited by the gas particles. For example, the value for the constant  $a$  for helium is 0.034, whereas that of water is 5.46. Thus, the correction factor for water, which exhibits hydrogen bonding, is much greater than that of helium, which exhibits the much weaker London dispersion forces.

Because the particles attract each other, we can surmise that at sufficiently low temperatures (or high pressures) the gas will condense. This behavior is demonstrated by considering a plot of pressure versus volume for a real gas at various temperatures.

A plot of  $P$  versus  $V$  for a gas behaving ideally is a hyperbola, as shown in Fig. 5.5. The shape of this plot will not change at different temperatures. But for a real gas, this is not the case.

Recall from studying phase diagrams in Chapter 10 that the critical temperature ( $T_c$ ) of a substance is the temperature above which the vapor cannot be liquefied no matter what pressure is applied. Let's look at how the  $P$  versus  $V$  plot changes for a real gas at temperatures above, at, and below the critical temperature.

Note that at temperatures above the critical temperature, the plots look similar to that of an ideal gas, although the shape changes as the temperature is lowered. At the critical temperature there is an inflection point, called the *critical point* (labeled  $C_p$  in Fig. A.9). Below the critical temperature we can see that there is a region where the pressure decreases with decreasing volume. This is because the gas is condensing. In the region between points 1 and 2, the substance is in liquid/vapor equilibrium. At volumes below 1, only liquid remains and the pressure increases as the liquid is compressed.

## A7.4 | Molecular Spectroscopy: An Introduction

Spectroscopy can be defined as the study of the interaction of electromagnetic radiation with matter. Spectroscopy provides a nondestructive and highly sensitive method for obtaining information about the identity, structure, and properties of substances. We have already discussed the emission spectrum of the hydrogen atom in Chapter 7 and the importance of the information it provides about hydrogen's quantized energy

levels. Spectroscopy is also very useful for the study of molecules. Molecules can absorb electromagnetic radiation to furnish energy for many different processes, all which have quantized energy levels.

For example, a molecule can absorb or emit a photon and go from a lower electronic energy state to a higher electronic energy state or vice versa. This "electronic transition" can be described approximately as a change from one electronic arrangement to another. Typically, electronic transitions require photons in the ultraviolet (UV) or visible regions of the spectrum. One example of the use of this type of spectroscopy is illustrated by photoelectron spectroscopy (PES) discussed in Section 9.6.

Molecules can also undergo vibrational energy transitions. For example, the atoms in a molecule vibrate around their equilibrium positions, giving rise to quantized vibrational energy levels. These spacings correspond to the energies of photons in the infrared (IR) region of the electromagnetic spectrum.

In addition, molecules can rotate, and the spacings of quantized rotational energy levels correspond to the energies of photons in the microwave region. In fact, it is the rotational excitation of the water molecules in food and the transfer of this energy to other molecules that form the basis of microwave cooking.

We will consider electronic spectroscopy and vibrational spectroscopy in more detail.

## Electronic Spectroscopy

The electronic spectrum of a molecule, which typically occurs in the ultraviolet (UV) or visible region of the electromagnetic spectrum, provides information about the spacings of electronic energy levels in the molecule. This allows us to better determine the electronic structure of a molecule. The electronic spectrum plots the quantity of radiation absorbed versus the wavelength of the radiation, showing peaks (maxima) at wavelengths where the photons have an energy that matches an energy gap in the molecule.

The majority of electronic transitions in molecules occurs in the UV region of the spectrum because the energy separations of electron states typically correspond to the energies of the photons in the UV region. However, some molecules have electronic energy separations that correspond to radiation in the visible region. One such class of compounds includes the coordination compounds that contain transitional metal ions. Thus, for example, dissolving copper(II) sulfate ions in water gives rise to a characteristic blue solution. Coordination compounds are discussed in Chapter 21. Another class of compounds that absorbs in the visible region of the spectrum involves molecules with long chains of carbon molecules that have alternating double bonds, such as carotene. The molecular structure of beta-carotene is given in Fig. A.10.

Substances with alternating double bonds are called *conjugated molecules*. It turns out that as the conjugated system gets longer, the electronic energies get closer together and the light absorbed corresponds to longer wavelengths.

White light consists of all of the colors of the rainbow (see Fig. 7.7), so when particular colors are absorbed by a given molecule, the substance appears colored. The color that results is the one given by the "sum" of the colors that remain unabsorbed. For example, carotene absorbs visible light in the violet and blue regions. It appears orange in color because the colors not absorbed "add up" to produce orange. In fact, carotene is the substance that gives carrots their bright orange color. The electronic absorption spectrum of beta-carotene is shown in Fig. A.11.

Electronic spectroscopy also provides a sensitive and accurate method for determining the amount of absorbing species present in a sample (quantitative analysis). This technique is described in Appendix 3.

## Vibrational Spectroscopy

As we have seen, a molecule can be approximated as a collection of atoms held together by bonds. In describing the vibrations in a molecule, we can compare the bond between a given pair of atoms to a spring attached to two masses. As the atoms move

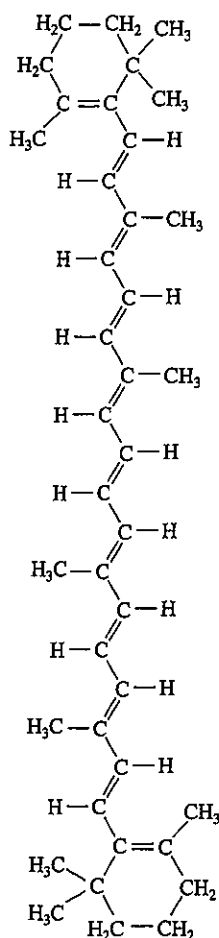
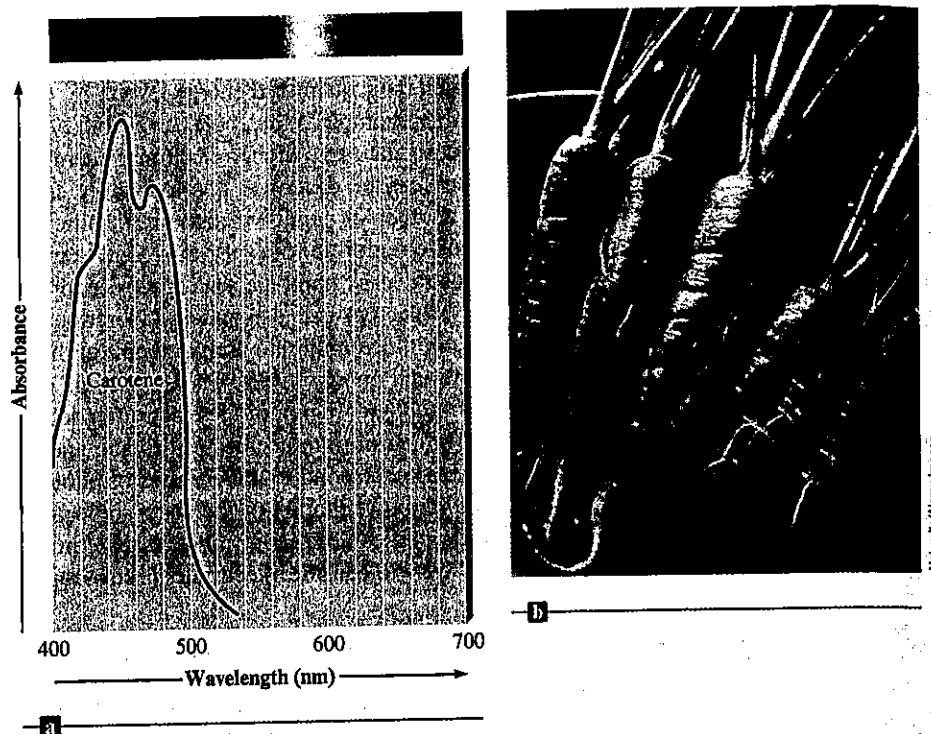


Figure A.10

Figure A.11



apart in a vibrational motion, the bond—like a spring—provides a restoring force that pulls the atoms back toward each other. Vibrational transitions in molecules usually require energies that correspond to the IR region of the electromagnetic spectrum. The data are often represented in “wave numbers;” a wave number is the reciprocal of the wavelength (in centimeters) required to cause the vibrational transition.

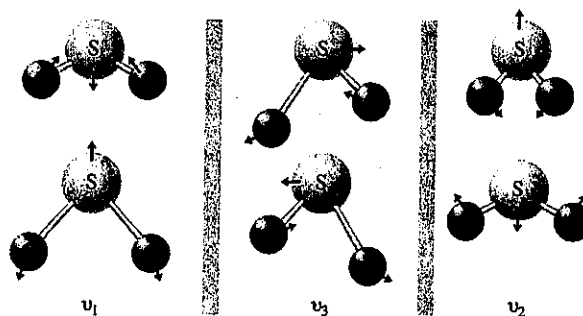
A particular bonded pair of atoms has a characteristic vibrational frequency (wave number) that is relatively insensitive to its molecular environment. Thus, a signal that appears in the IR spectrum at that characteristic frequency provides good evidence that this particular atom pair is present in the molecule. For example, a C—H pair in a molecule will always show a vibrational signal at about  $3000\text{ cm}^{-1}$  (the range of wave numbers is actually  $2850\text{--}3300\text{ cm}^{-1}$  depending on the specific molecular environment). On the other hand, the O—H group in a molecule will show a vibrational bond at about  $3600\text{ cm}^{-1}$ . Typical frequency ranges for the stretching motions of several common bonds are given in the table below.

Bond	Frequency Range ( $\text{cm}^{-1}$ )
C—H	2850–3300
C=C	1640–1680
C≡C	2100–2260
C—O	1080–1300
C=O	1690–1760
O—H	3610–3640

It turns out that several characteristic vibrational motions, called *normal modes*, are possible, not simply stretching motions. As an example, the normal modes of vibration for the  $\text{SO}_2$  molecule are shown in Fig. A.12.

The IR spectrum of a molecule can be a great aid in identifying which atom groupings (that is, the types of bonds) are present in a molecule and thus can provide valuable information for identifying a specific molecule.

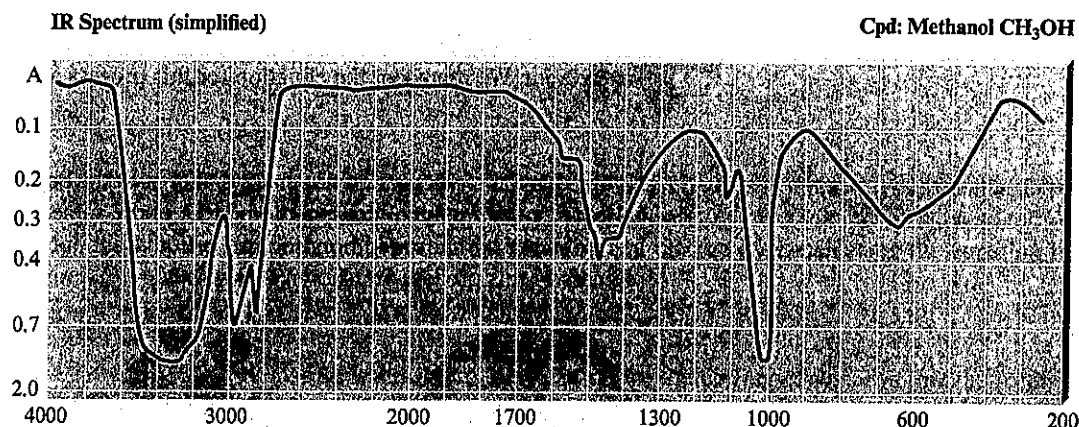
Figure A.12



For example, consider methanol ( $\text{CH}_3\text{OH}$ ), which has the following structure:



The IR spectrum of methanol is:



Notice that we can identify the bond present due to the stretching motions. The spectrum has other peaks due to different modes of vibration (such as those we saw with the  $\text{SO}_2$  molecule) and hydrogen bonding between the molecules.

## A7.5 | Intermolecular Forces Between Polar and Nonpolar Molecules

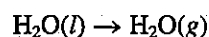
In Chapter 10 we discussed intermolecular forces between polar molecules (dipole-dipole interactions) and intermolecular forces between nonpolar molecules (London dispersion forces; these forces exist between polar molecules as well but are not as strong as the dipole-dipole interactions). In addition, polar molecules and nonpolar molecules exhibit an attraction for one another. Recall from Chapter 10 that a nonpolar molecule can form an instantaneous dipole that can induce a similar dipole in a neighboring molecule. Similarly, a permanent dipole on a polar molecule can induce a dipole on a neighboring nonpolar molecule. This is termed a dipole-induced dipole interaction. The strength of this interaction depends on the natures of both the polar molecule and the nonpolar molecule. The larger the magnitude of the dipole in a polar molecule, the better able it is to induce a dipole in a neighboring molecule. Just as we discussed with London dispersion forces, nonpolar molecules with a greater number of electrons have an increased polarizability, therefore increasing the ease with which a dipole is induced.

## A7.6 | Distinguishing Between Chemical and Physical Changes at the Molecular Level

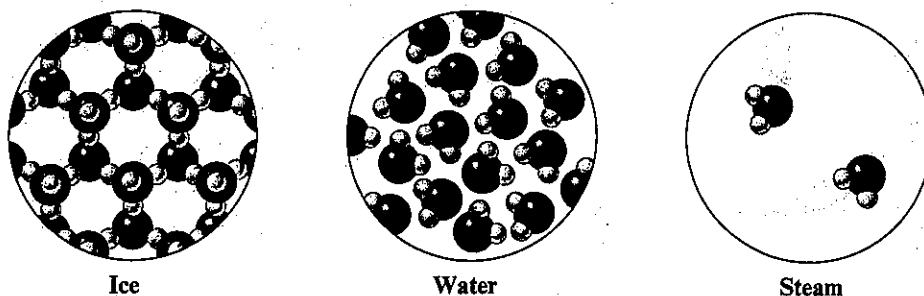
In Chapter 1 we defined physical and chemical changes mostly from a macroscopic perspective. A physical change was noted as a change in the form of the substance, but not in its chemical composition. A chemical change was defined as a change of substances into other substances with different properties and different composition. After studying Chapters 8, 9, and 10, we can look at these changes at the molecular level.

In Chapters 8 and 9 we discussed the forces holding atoms together as molecules. These *intramolecular* (within the molecule) forces are termed *chemical bonds*. In Chapter 10 we considered *intermolecular* forces, or the forces that exist between molecules. Determining whether a process comes about because of disruption of intramolecular forces or intermolecular forces allows us to distinguish between chemical and physical changes.

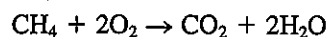
A typical example of a physical change is a phase change, such as the boiling of water. In this process, energy as heat is transferred to liquid water and the intermolecular forces (hydrogen bonding in this case) are overcome, resulting in the formation of water vapor. We represent the equation for this process as:



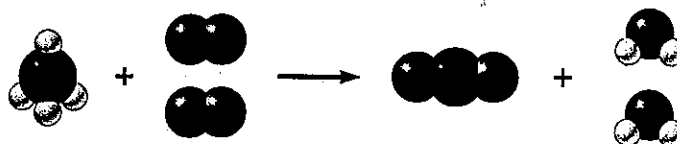
Notice that the molecules do not change; that is, at the beginning and end of the physical change the chemical composition,  $\text{H}_2\text{O}$ , is the same. However, the molecules are held together by hydrogen bonding in the liquid but not in the vapor. Molecular level pictures of this process are shown below:



So the change of water from the liquid to the gaseous phase is a physical process, because the  $\text{H}_2\text{O}$  molecules remain intact during the process. If a process results by breaking and/or forming chemical bonds (or intramolecular forces), the process is a chemical change. For example, consider the combustion of methane ( $\text{CH}_4$ ) to form carbon dioxide and water. The balanced equation is



For this reaction to occur, the chemical bonds between carbon and hydrogen in methane and between the oxygen atoms in diatomic oxygen must be broken, and chemical bonds between the carbon and oxygen in carbon dioxide and hydrogen and oxygen in water must be formed. Molecular level pictures of this process are shown below:



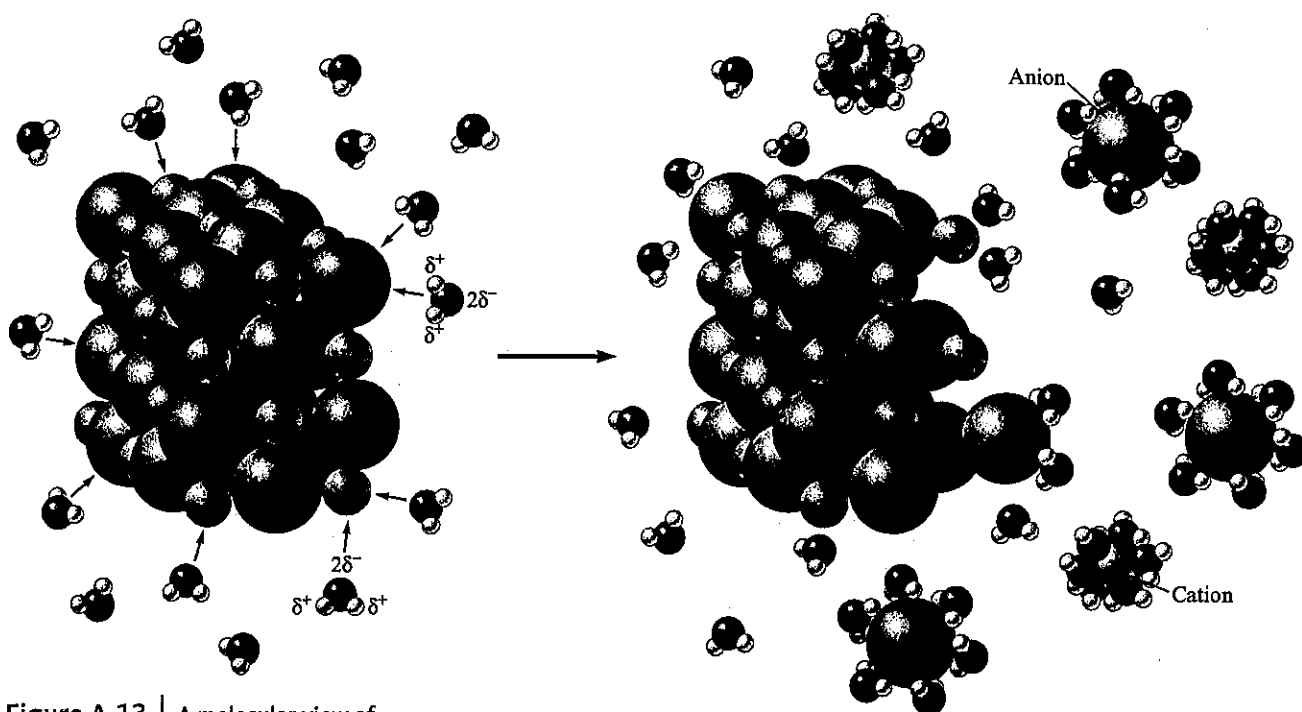


Figure A.13 | A molecular view of an ionic salt dissolving in water.

The distinction between physical and chemical changes is not always as clear as in the previous examples. For example, consider dissolving table salt,  $\text{NaCl}(s)$ , in water. We can make an argument that this is a physical change by considering the equation for the process:



This equation is similar to the equation for the boiling of water in that the formula for the reactant and product is the same while only the form changes. It would appear, then, that the process of an ionic solid dissolving is a physical change. However, this conclusion is not as obvious if we look at a molecular view of the process, shown in Fig. A.13.

For  $\text{NaCl}$  to go into solution, the ionic bonds holding the  $\text{Na}^+$  and  $\text{Cl}^-$  together must be broken. In addition, interactions are formed between the ions and the water molecules. The strength of these forces (especially the ionic bonds) can be similar to the strengths of covalent chemical bonds. From this perspective, we could argue that this process is a chemical change.

Thus, a molecular-level perspective can help us distinguish between chemical and physical changes by considering whether intramolecular or intermolecular forces are disrupted. However, we need to be careful to not oversimplify the issue, because some processes fall in a gray area between a purely chemical change and a purely physical change.

## A7.7 | Intermolecular Forces and Thermodynamics: Why Aren't All Ionic Solids Soluble in Water?

In Chapter 11 we discussed the concept of *like dissolves like*. This implies that an ionic solute [such as table salt,  $\text{NaCl}(s)$ ] should dissolve in a polar solvent [such as water]. The process of forming a solution was given as a series of three steps as shown in



Figs. 11.1 and 11.2, and the overall  $\Delta H_{\text{soln}}^\circ$  for dissolving  $\text{NaCl}(s)$  in water was found to be positive (requires energy). Recall from Chapter 17 that to predict whether a given process (at constant temperature and pressure) is spontaneous, we must consider the change in free energy:

$$\Delta G = \Delta H - T\Delta S$$

It is an experimental fact that  $\text{NaCl}(s)$  dissolves in water to form 1.0 M  $\text{NaCl}$ . Thus,  $\Delta G^\circ$  for this process must be negative. Since  $\Delta H_{\text{soln}}^\circ$  is positive and unfavorable,  $\Delta S_{\text{soln}}^\circ$  must be positive and large enough to make  $\Delta G^\circ$  negative (through the  $-T\Delta S^\circ$  term). It is certainly not surprising that  $\Delta S_{\text{soln}}^\circ$  would be positive for this process. In considering the three steps of dissolution of a solute mentioned in Chapter 11, we would expect  $\Delta S_1$  and  $\Delta S_2$  to be positive since the solute and solvent are “expanded” in these steps. Also,  $\Delta S_3$  would be expected to be positive in a general case because a solute is randomly dispersed in the relatively large volume of solvent.

Thus, we might generalize for an ionic (or polar) solute dissolving in a polar solvent as follows: because  $\Delta H_{\text{soln}}^\circ$  contains large positive and negative contributions, it is difficult to predict the sign of  $\Delta H_{\text{soln}}^\circ$ . However, even if  $\Delta H_{\text{soln}}^\circ$  is positive, it is not expected to be so large that it would overwhelm the expected positive value of  $\Delta S_{\text{soln}}^\circ$  for this process. The overall effect is to make  $\Delta G_{\text{soln}}^\circ$  negative, thus the solution forms spontaneously.

However, as we noted in Chapter 10, water is not a typical liquid, with most of its unusual properties arising from the extensive hydrogen bonding present among the molecules. Because of water’s unique nature, we must be very cautious in using simple arguments to account for the solvent properties of water.

To illustrate the unusual nature of water as a solvent, consider the following values of  $\Delta S_{\text{soln}}^\circ$  for  $\text{KCl}(s)$ ,  $\text{LiF}(s)$ , and  $\text{CaS}(s)$  forming aqueous solutions.

$\text{KCl}(s) \rightarrow \text{K}^+(aq) + \text{Cl}^-(aq)$	75
$\text{LiF}(s) \rightarrow \text{Li}^+(aq) + \text{F}^-(aq)$	-36
$\text{CaS}(s) \rightarrow \text{Ca}^{2+}(aq) + \text{S}^{2-}(aq)$	-138

Note that when  $\text{KCl}(s)$  is dissolved in water to form a 1.0 M solution, the value of  $\Delta S_{\text{soln}}^\circ$  is positive, as expected from the previous discussion. However, note that  $\Delta S_{\text{soln}}^\circ$  is *negative* for the other two salts. Why? How could the random dispersal in water of ions formerly present in a highly ordered solid produce a negative entropy change?

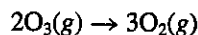
Obviously, something must be occurring in the solution process that leads to increased order, which in some cases is large enough to dominate  $\Delta S_{\text{soln}}^\circ$ . There is little doubt that this ordering effect arises from the hydration of the ions. In describing aqueous solutions containing ionic solutes in Chapter 4, we discussed the fact that the polar water molecules are attracted to the ions to form hydrated species. The assembling of a group of water molecules around the ions is an order-producing phenomenon and would be expected to make a negative contribution to  $\Delta S_{\text{soln}}^\circ$ . Studies show that the more charge density an ion possesses, the greater this hydration effect will be. This idea is borne out by the data in the table above. For example, note that  $\Delta S_{\text{soln}}^\circ$  for  $\text{KCl}(s)$  is positive, but the value for  $\text{LiF}(s)$  is negative. This probably results from the smaller sizes (and larger charge densities) of  $\text{Li}^+$  and  $\text{F}^-$  compared with  $\text{K}^+$  and  $\text{Cl}^-$ . The smaller ions presumably are able to bind to the hydrating water molecules more firmly and thus show a more negative value for  $\Delta S_{\text{soln}}^\circ$ . The charges on the ions are also important. Note that  $\text{CaS}(s)$  exhibits a value for  $\Delta S_{\text{soln}}^\circ$  that is more negative than that for  $\text{LiF}(s)$ , as might be expected for the more highly charged  $\text{Ca}^{2+}$  and  $\text{S}^{2-}$  ions.

As we can see, enthalpy changes alone are not enough to predict solubility—we must also consider entropic effects. However, the dissolution process is so complex

that successfully predicting whether a particular solute will dissolve in a given solvent is almost impossible. The only way to be certain about the solubility of a given solute in a solvent is to do the experiment.

## A7.8 | Mechanisms with Fast Forward and Reverse First Steps

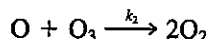
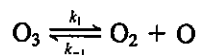
A common type of reaction mechanism is one involving a first step in which *both* the forward and reverse reactions are very fast compared with the reactions in the second step. An example of this type of mechanism is that for the decomposition of ozone to oxygen. The balanced reaction is



The observed rate law is

$$\text{Rate} = k \frac{[\text{O}_3]^2}{[\text{O}_2]}$$

Note that this rate law is unusual in that it contains the concentration of a *product*. The mechanism proposed for this process is



The double arrows in the first step indicate that both the forward and reverse reactions are important. They have the rate constants  $k_1$  and  $k_{-1}$ , respectively.

For this mechanism we will assume that *both* the forward and reverse reactions of the first step are very fast compared with the reaction in the second step. This means that the second step is rate determining. Therefore, the rate for the overall reaction is equal to the rate of the second step:

$$\text{Rate} = k_2[\text{O}][\text{O}_3]$$

This rate law does not have the same form as the experimentally determined rate law. For one thing, it contains the concentration of the intermediate, an oxygen atom. We can remove  $[\text{O}]$  and obtain a rate law that agrees with the experiment results by making an additional assumption. We assume that the rates of the forward and reverse reactions in the first step are equal. That is, we assume that the initial reversible fast step is at equilibrium. This makes sense because the rates of both the forward and reverse reactions for the first step are so much faster than the rate of the second step. For the first step,

$$\text{Rate of forward reaction} = k_1[\text{O}_3]$$

and

$$\text{Rate of reverse reaction} = k_{-1}[\text{O}_2][\text{O}]$$

At equilibrium we have

$$k_1[\text{O}_3] = k_{-1}[\text{O}_2][\text{O}]$$

We solve for  $[\text{O}]$ :

$$[\text{O}] = \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2]}$$

The second step is relatively slow because of the very small concentration of  $\text{O}_3$  molecules.

Now we substitute the expression for  $[O]$  into the rate law for the second step:

$$\begin{aligned}\text{Rate} &= k_2[O_2][O_3] = k_2\left(\frac{k_1[O_3]}{k_{-1}[O_2]}\right)[O_3] = \frac{k_2k_1[O_3]^2}{k_{-1}[O_2]} \\ &= k\frac{[O_3]^2}{[O_2]}\end{aligned}$$

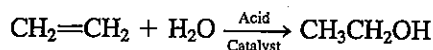
where  $k$  is a composite constant representing  $k_2k_1/k_{-1}$ .

This rate law, *derived* by postulating the two elementary steps and making assumptions about the relative rates of these steps, agrees with the experimental rate law. Since this mechanism (the elementary steps *plus* the assumptions) also gives the correct overall stoichiometry, it is an acceptable mechanism for the decomposition of ozone to oxygen.

## A7.9 | Acid Catalysis

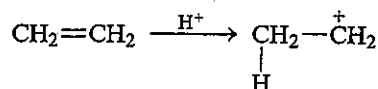
In Section 12.7 you learned that a catalyst is a substance that speeds up a reaction without being consumed itself. Acids and bases can serve as catalysts in chemical reactions. In acid-catalyzed reactions, for example, a reactant gains a proton ( $H^+$ ). The  $H^+$  ion, being positively charged, is attracted to the lone pairs on atoms such as O, N, or S in a molecule, or to  $\pi$  bonds in an alkene or alkyne.

For example, in Chapter 22 you saw that a common industrial method for the production of ethanol is the acid-catalyzed reaction of ethylene and water:

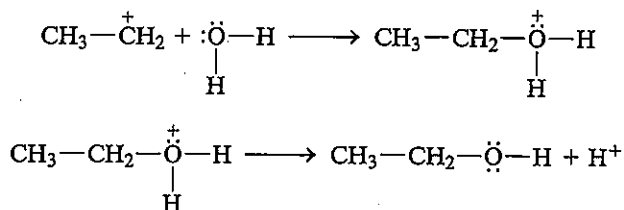


In this case, the  $H^+$  is attracted to the double bond on ethylene to make a new intermediate that is very reactive. This provides for a new pathway for the reaction that has lower activation energy and therefore proceeds more quickly than without the addition of the acid catalyst.

The mechanism for this reaction can be represented as follows:



Because the carbon atom on the right side of the product written above does not have an octet of electrons, the product is more reactive with water than is ethylene. The reaction proceeds as follows:



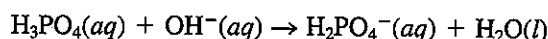
Notice that  $H^+$  is a product of the final reaction in the mechanism. Although it is not the same hydrogen ion that catalyzed the reaction, there is not a net consumption of  $H^+$  in the overall reaction.

## A7.10 | Polyprotic Acid Titrations

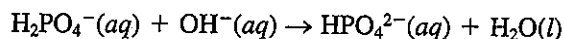
In Chapter 14 we discussed polyprotic acids, or acids that can furnish more than one proton. Acid-base titrations were covered in Chapter 15, but these involved only monoprotic acids. When a polyprotic acid is titrated, the pH curve has similar features to those of a monoprotic acid, but enough differences exist to warrant special coverage.

Recall from Chapter 14 that a polyprotic acid dissociates in a stepwise manner, one proton at a time. In a titration of a polyprotic acid, the various acidic protons are titrated in succession as well.

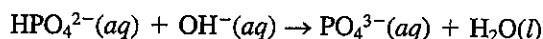
For example, as sodium hydroxide is used to titrate phosphoric acid, the first reaction that takes place can be represented as



This reaction occurs until the  $\text{H}_3\text{PO}_4$  is consumed (to reach the first equivalence point). Therefore, at the first equivalence point the solution contains the major species  $\text{Na}^+$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{H}_2\text{O}$ . Then, as more sodium hydroxide is added, the reaction



occurs to give a solution that contains  $\text{Na}^+$ ,  $\text{HPO}_4^{2-}$ , and  $\text{H}_2\text{O}$  as the major species at the second equivalence point. As sodium hydroxide is added beyond the second equivalence point, the reaction that occurs can be represented as



Although we will not fully discuss the calculations involved in obtaining the pH curve for a polyprotic acid, the calculations are closely related to those for a monoprotic acid. The same principles apply, but we must be very careful in identifying which of the various equilibria is appropriate to use in a given case. The secret to success here is, as always, identifying the major species in solution at any given point in the titration. We summarize the various cases in Table A.2 for a triprotic acid  $\text{H}_3\text{A}$  with dissociation constants  $K_{a1}$ ,  $K_{a2}$ , and  $K_{a3}$ .

Recall from Chapter 15 that at the halfway point in the titration of a monoprotic weak acid with a strong base, the pH of the solution is equal in value to the  $\text{p}K_a$  of the weak acid. Through similar reasoning, it turns out that we can use a pH curve for the titration of a polyprotic acid with a strong base to determine the  $K_a$  values of the given acid. We can see this in a pH curve for the titration of the generic triprotic acid  $\text{H}_3\text{A}$  with  $\text{NaOH}$  (Fig. A.14).

Note that the pH can be easily determined at the first two equivalence points by using the average of the corresponding  $\text{p}K_a$  values. It turns out as well that the pH values at the half-equivalence points can be estimated as equal to the corresponding  $\text{p}K$  values. Thus,  $\text{pH} \approx \text{p}K_{a1}$  for the first half-equivalence point,  $\text{pH} \approx \text{p}K_{a2}$  at the second half-equivalence point, and  $\text{pH} \approx \text{p}K_{a3}$  at the third half-equivalence point.

We can also use pH curves to easily determine the number of acidic protons on a particular acid. In Chapter 15 you saw that the pH curve for the titration of a monoprotic acid (one acidic proton,  $\text{HA}$ ) has one equivalence point. The previous discussion shows that a pH curve for a triprotic acid (three acidic protons,  $\text{H}_3\text{A}$ ) has three equivalence points. As expected, the pH curve for the titration of a diprotic acid (two acidic

Table A.2 | A Summary of Various Points in the Titration of a Triprotic Acid

Point in the titration	Major Species
No base added	$\text{H}_3\text{A}$ , $\text{H}_2\text{O}$
Base added	
Before the first equivalence point	$\text{H}_3\text{A}$ , $\text{H}_2\text{A}^-$ , $\text{H}_2\text{O}$
At the first equivalence point	$\text{H}_2\text{A}^-$ , $\text{H}_2\text{O}$
Between the first and second equivalence points	$\text{H}_2\text{A}^-$ , $\text{HA}^{2-}$ , $\text{H}_2\text{O}$
At the second equivalence point	$\text{HA}^{2-}$ , $\text{H}_2\text{O}$
Between the second and third equivalence points	$\text{HA}^{2-}$ , $\text{A}^{3-}$ , $\text{H}_2\text{O}$
At the third equivalence point	$\text{A}^{3-}$ , $\text{H}_2\text{O}$
Beyond the third equivalence point	$\text{A}^{3-}$ , $\text{OH}^-$ , $\text{H}_2\text{O}$

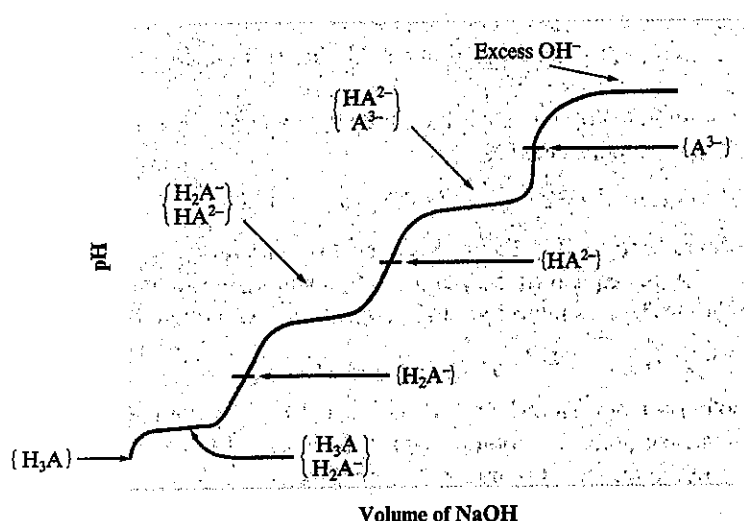


Figure A.14

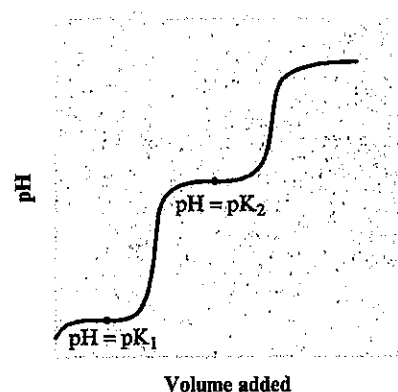


Figure A.15

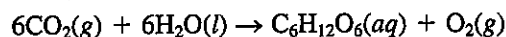
protons,  $H_2A$ ) has two equivalence points. A typical pH curve for the titration curve for a diprotic acid is given in Fig. A.15.

Note that we can determine the pH values at various points on the curve by using the appropriate  $pK_a$  values, just as we saw with the titration of a triprotic acid.

## A7.11 | Non-Spontaneous Reactions

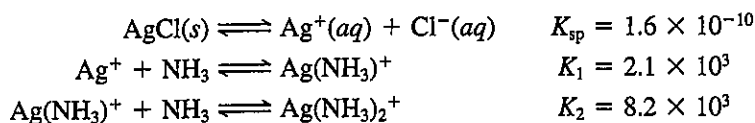
In Chapter 17 we saw that in order for a reaction to be spontaneous, the value of  $\Delta G$  must be less than zero (negative) at constant pressure and temperature. But reactions for which  $\Delta G > 0$  can be made to proceed. We can cause these so-called thermodynamically unfavorable reactions to occur by either applying external energy or by coupling these unfavorable reactions to thermodynamically favorable ones.

For example, we saw in Chapter 18 that we can use electrical energy to produce a chemical change by means of an electrolytic cell. In addition, electromagnetic radiation may be used because the absorption of photons can initiate a reaction. This is what happens when carbon dioxide is converted to glucose through photosynthesis:

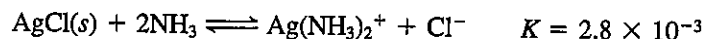


For this reaction,  $\Delta G^\circ = +2880 \text{ kJ/mol}$ , making it thermodynamically unfavorable. However, light energy is used to initiate a series of steps that provide energy to carry out the reaction above. Note, then, that it is not the light energy itself that is used to carry out the reaction. For example, in photosynthesis, the absorption of photons in the visible range causes the formation of adenosine triphosphate (ATP) from adenosine diphosphate (ADP). When the plant converts ATP back to ADP, a great deal of energy is released, which is then used to convert carbon dioxide to glucose. Thus, a thermodynamically favorable reaction drives the thermodynamically unfavorable reaction. We say these reactions are coupled. Many biological systems use the energy derived from the conversion of ATP to ADP to run thermodynamically unfavorable reactions.

For reactions to be coupled, the reactions must have common intermediates. We have seen this idea in Section 16.3 when considering the dissolving of  $AgCl(s)$  in  $NH_3$ . The series of relevant reactions are:



The overall reaction is given as:



where  $K = K_{sp} \times K_1 \times K_2$ .

We can see that the dissolution of  $\text{AgCl}(s)$  in water (as shown in the first reaction in the series) is very unfavorable. Recall from Chapter 17 that  $\Delta G^\circ = -RT \ln(K)$ . Thus, for  $\text{AgCl}(s)$  dissolving in water,  $\Delta G^\circ = +55.9 \text{ kJ/mol}$ , which is thermodynamically unfavorable.

For the second and third reactions in the series,  $\Delta G^\circ = -19.0 \text{ kJ/mol}$  and  $-22.3 \text{ kJ/mol}$ , respectively. These reactions are thermodynamically favorable.

For the overall reaction of dissolving  $\text{AgCl}(s)$  in  $\text{NH}_3$ ,  $\Delta G^\circ = +14.6 \text{ kJ/mol}$ . Although this is still not thermodynamically favorable, it is more favorable (that is, less positive) than the reaction of dissolving  $\text{AgCl}(s)$  in water.

We can also drive the overall reaction to the right by using an excess of  $\text{NH}_3$ , as described by Le Châtelier's principle. As seen in Section 16.3, the solubility of  $\text{AgCl}(s)$  in  $\text{NH}_3$  is more than 36,000 times as soluble in  $10.0 \text{ M NH}_3$  as it is in water. Thus, even though the reaction is thermodynamically unfavorable, we can still obtain a relatively large amount of products depending on our initial conditions.